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Characterization of Post-Fire Priming Cup Residue Using Scanning Electron Microscopy Coupled With Energy Dispersive X-Ray Spectrometry

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CHARACTERIZATION OF POST-FIRE PRIMING CUP RESIDUE USING SCANNING ELECTRON MICROSCOPY COUPLED WITH ENERGY DISPERSIVE X-RAY SPECTROMETRY

by

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ABSTRACT

Ammunition is most often comprised of a lead-based priming mixture which contributes to the traditional characteristics of gunshot residue (GSR). Due to the health risks often associated with lead, lead-free primer alternatives are becoming increasingly more popular. Thus, it is becoming more difficult to determine the presence of GSR based on traditional means, i.e. the presence of lead (Pb), barium (Ba), and antimony (Sb). Eight different ammunitions were purchased which consisted of one lead-based and one lead-free from four different manufacturers, including Winchester, Federal, Liberty, and Sellier & Bellot. Half of the rounds from each manufacturer and chemical composition (i.e. lead-based or lead-free) were disassembled, e.g. the projectile and smokeless powder were removed, leaving the priming cup in place (i.e. primed only). The remaining cartridges were left intact (i.e. full cartridge). Both the full cartridges and the primed only cartridges for each ammunition were fired using a 9mm Glock and the cartridges were collected post-fire, and subsequently deprimed.

Five cups and five anvils from each type of ammunition were adhered to aluminum stubs via colloidal graphite. The GSR remaining on the anvils and in the cups was then analyzed using scanning electron microscopy coupled with energy dispersive x-ray spectrometry (SEM-EDX). Three spectra were collected for each anvil and each cup resulting in 30 total spectra per type of ammunition. The primary element peaks were then selected and four different dataset matrices were created for the full cartridge anvils, full cartridge cups, primed only anvils, and primed only cups. The data was processed using unit vector normalization and was then

analyzed using principal component analysis (PCA) and linear discriminant analysis (LDA) to determine the characterization between lead-free and lead-based ammunition.

The anvils provided better separation and characterization based on the ability to better collect x-rays, and therefore demonstrated the capability of the ammunition to cluster by both primer mixture composition and manufacturer. The lead-based and lead-free primers showed consistencies across samples, such as the presence or absence of K, which allowed for characterization based on primer composition.

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TABLE OF CONTENTS

LIST OF FIGURES xi

LIST OF TABLES xviii

LIST OF ABBREVIATIONS (or) ACRONYMS xix

CHAPTER 1: INTRODUCTION 1

CHAPTER 2: LITERATURE REVIEW 4

2.1 Ammunition 4

2.2 Gunshot Residue Formation 9

2.3 Gunshot Residue Identification 13

2.4 Sources of Residue Similar to Gunshot Residue 15

2.5 Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM-EDX) 16

2.5.1 Scanning Electron Microscope (SEM) 17

2.5.2 Energy Dispersive X-ray Spectrometer (EDX) 20

2.6 Other Laboratory Testing 25

2.7 Field Tests 26

2.8 Sample Preparation 27

2.8.1 Sample Collection 27

2.8.2 Sample Coating 29

CHAPTER 3: METHODS 33

3.1 Samples 33

3.2 Sample Preparation 34

3.3 SEM-EDX Analysis 35

3.4 Muzzle Discharge 37

CHAPTER 4: STATISTICAL ANALYSIS 38

4.1 Data Normalization 38

4.2 Principal Component Analysis 41

4.2.1 Background 41

4.2.2 Data Analysis 42

4.3 Linear Discriminant Analysis 44

4.3.1 Data Analysis 44

CHAPTER 5: RESULTS AND DISCUSSION 46

5.1 Residue Images 47

5.2 Lead-Based Ammunition Spectra 50

5.2.1 Federal Lead-Based 50

5.2.2 Liberty Lead Based 53

5.2.3 Winchester Lead-Based 56

5.2.4 Sellier & Bellot Lead-Based 59

5.3 Lead-Free Ammunition Spectra 62

5.3.1 Federal Lead-Free 62

5.3.2 Liberty Lead-Free 65

5.3.3 Winchester Lead-Free 68

5.3.4 Sellier & Bellot Lead-Free 71

5.4 Spectral Comparisons 74

5.5 Principal Component Analysis 76

5.5.1 Full Cartridge Anvils 76

5.5.2 Primed Only Anvils 80

5.5.3 Full Cartridge Cups 84

5.5.4 Primed Only Cups 89

5.6 Linear Discriminant Analysis 95

5.7 Muzzle Discharge Residue 99

5.7.1 EDX Spectra 99

5.7.2 Principal Component Analysis 103

CHAPTER 6: CONCLUSIONS AND FUTURE WORK 109

6.1 Conclusions 109

6.2 Future Work 112

APPENDIX A: ELEMENTAL ENERGIES 113

APPENDIX B: SEM IMAGES ANVILS AND CUPS 115

APPENDIX C: SEM IMAGES MUZZLE DISCHARGE 132

REFERENCES 135

LIST OF FIGURES

Figure 1: Schematic diagram of ammunition[1] 4

Figure 2: Primer pocket diagram[4] 6

Figure 3: Designs of bullets 8

Figure 4: Schematic diagram of the scanning electron microscope 18

Figure 5: Bohr model of the atom 21

Figure 6: A) A schematic showing the general set-up of an EDX detector. B) The schematic of the detector used in this project 22

Figure 7: A) Aluminum scanning electron microscope mounts B) Carbon adhesive tabs C) Liquid adhesive composed of colloidal graphite in an isopropanol base 28

Figure 8: Example of samples prepared for SEM-EDX analysis 29

Figure 9: EDS Spectra for a particle from the Federal Lead based ammunition. The carbon peak appears to the far left of the spectra rather than overlapping with the key elements, i.e. Pb, Ba, and Sb. 30

Figure 10: Pictured above is the Denton Sputter/Coater. The instrument to the left is used for the sputter/coating of Au/Pd, while the instrument to the right is the additional carbon accessory for thermal evaporation. 31

Figure 11: A) Harvey Depriming tool used for most of the cartridge cases B) Lee Reloading Press using for those cartridge cases which had a small flash hole 35

Figure 12: A) LEO 1450 VP SEM located at NCFS B) JEOL JSM-640LV SEM located at AMPAC 36

Figure 13: Raw spectral data condensed into one workbook per ammunition. This workbook corresponds to the Federal Lead-based ammunition. The letter in each column header designates the anvil or cup number while the number indicates the spectra number ... 39
Figure 14: This shows the raw spectral data once it has been peak picked. The data on the left shows the intensities for the significant signals. The data on the right shows the data peak picked based on its correlation to specific elements. ... 40
Figure 15: A) PC scores plot showing the data for the full cartridge cups separated by their priming mixture, i.e. lead-free or lead-based. B) PC scores plot showing the data for the full cartridge cups separated by manufacturer. ... 43
Figure 16: A) PC scores plot showing the data for the full cartridge anvils separated based on their priming mixture, i.e. lead-free or lead-based. B) PC scores plot showing the separation of data based on manufacturer. ... 43
Figure 17: Lead-Based residue on the base of the priming cups. The numbers indicate the particles from which spectra were collected. A) Federal B) Sellier & Bellot C) Winchester D) Liberty ... 47
Figure 18: Lead-Free Residue on the base of the priming cups. The numbers indicate the particles from which spectra were collected. A) Federal B) Sellier & Bellot C) Winchester D) Liberty ... 48
Figure 19: A) EDX spectra for the Federal lead-based full cartridge anvils B) EDX spectra for the Federal lead-based full cartridge cups ... 51

Figure 20: A) EDX spectra for the Federal lead-based primed only anvils B) EDX spectra for the Federal lead-based primed only cups 52
Figure 21: A) EDX spectra Liberty lead-based full cartridge anvils B) EDX spectra for Liberty lead-based full cartridge cups 54
Figure 22: A) EDX spectra for Liberty lead-based primed only anvils B) EDX spectra for Liberty lead-based primed only cups 55
Figure 23: A) EDX spectra for Winchester lead-based full cartridge anvils B) EDX spectra for Winchester lead-based full cartridge cups 57
Figure 24: A) EDX spectra for Winchester lead-based primed only anvils B) EDX spectra for Winchester lead-based primed only cups 58
Figure 25: A) EDX spectra for Sellier & Bellot lead-based full cartridge anvils B) EDX spectra for Sellier & Bellot lead-based full cartridge cups 60
Figure 26: A) EDX spectra for Sellier & Bellot lead-based primed only anvils B) EDX spectra for Sellier & Bellot lead-based primed only cups 61
Figure 27: A) EDX spectra for Federal lead-free full cartridge anvils B) EDX spectra for Federal lead-free full cartridge cups 63
Figure 28: A) EDX spectra for Federal lead-free primed only anvils B) EDX spectra for Federal lead-free primed only cups 64
Figure 29: A) EDX spectra for Liberty lead-free full cartridge anvils b) EDX spectra for Liberty lead-free full cartridge cups 66

Figure 30: A) EDX spectra for Liberty lead-free primed only anvils B) EDX spectra for Liberty lead-free primed only cups 67
Figure 31: A) EDX spectra Winchester lead-free full cartridge anvils B) EDX spectra for Winchester lead-free full cartridge cups 69
Figure 32: A) EDX spectra for Winchester lead-free primed only anvils B) EDX spectra for Winchester lead-free primed only cups 70
Figure 33: A) EDX spectra for Sellier & Bellot lead-free full cartridge anvils B) EDX spectra for Sellier & Bellot lead-free full cartridge cups 72
Figure 34: A) EDX spectra for Sellier & Bellot lead-free primed only anvils B) EDX spectra for Sellier & Bellot lead-free primed only cups 73
Figure 35: PCA scores plots, using the first three PCs A) shows the distribution of ammunition based on the LBP or LFP mixture B) shows the distribution of ammunition based on manufacturer 78
Figure 36: A) Factor loadings plot for PC1 B) Factor loadings plot for PC2 79
Figure 37: PCA scores plots, using the first three PCs A) shows the distribution of ammunition based on the LBP or LFP mixture B) shows the distribution of ammunition based on manufacturer 82
Figure 38: A) Factor loadings plot for PC1 B) Factor loadings plot for PC2 83
Figure 39: PC scores plot using the first three PCs, highlights the distribution of scores on PC1 A) PC scores plot by the priming mixture, i.e. lead-based or lead-free B) PC scores plot by manufacturer 86

Figure 40: PC scores plots using the first three PCs, highlights the distribution of scores on PC2 and PC3 A) PC scores plot by the priming mixture, i.e. lead-bead or lead-free B) PC scores plot by manufacturer 87
Figure 41: A) Factor loadings for PC1 B) Factor loadings for PC2 C) Factor loadings for PC3 89
Figure 42: PC scores plot using the first three PCs, highlights the distribution of scores on PC1 A) PC scores plot by the priming mixture, i.e. lead-based or lead-free B) PC scores plot by manufacturer 92
Figure 43: PC scores plots using the first three PCs, highlights the distribution of scores on PC2 and PC3 A) PC scores plot by the priming mixture, i.e. lead-bead or lead-free B) PC scores plot by manufacturer 93
Figure 44: A) Factor loadings for PC1 B) Factor loadings for PC2 C) Factor loadings for PC3 95
Figure 45: Confusion matrices summarizing assignments of the samples classified with 5-fold cross-validation LDA for A) the full cartridge anvils B) primed only anvils C) and a combined matrix of the full and primed only cartridge datasets 97
Figure 46: Confusion matrices of the samples classified based on the previously created models for A) the full cartridge anvils B) the primed only anvils C) and the combined matrix of the full and primed only cartridge datasets 98
Figure 47: A) Sellier & Bellot lead-free full cartridge anvils with muzzle discharge B) Sellier & Bellot lead-free primed only anvils with muzzle discharge. 101
Figure 48: A) Winchester lead-based full cartridge anvils with muzzle discharge. B) Winchester lead-based primed only anvils with muzzle discharge. 102

Figure 49: PC scores plot using the first three PCs, highlights the distribution of anvils against the muzzle discharge residue A) PC scores plot for the full cartridge ammunition B) PC scores plot for the primed only ammunitions 106
Figure 50: Factor loadings for the full cartridge anvils with muzzle discharge A) Factor loadings for PC1 B) Factor loadings for PC2 107
Figure 51: Factor loadings for the primed only anvils with muzzle discharge A) Factor loadings for PC1 B) Factor loadings for PC2 108
Figure 52: Federal Lead-Based Anvils A) Full Cartridge B) Primed Only 116
Figure 53: Federal Lead-Based Cups A) Full Cartridge B) Primed Only 117
Figure 54: Liberty Lead-Free Anvils A) Full Cartridge B) Primed Only 118
Figure 55: Liberty Lead- Free Cups A) Full Cartridge B) Primed Only 119
Figure 56: Sellier & Bellot Lead-Free Anvils A) Full Cartridge B) Primed Only 120
Figure 57: Sellier & Bellot Lead-Free Cups A) Full Cartridge B) Primed Only 121
Figure 58: Sellier & Bellot Lead-Based Anvils A) Full Cartridge B) Primed Only 122
Figure 59: Sellier & Bellot Lead-Based Cups A) Full Cartridge B) Primed Only 123
Figure 60: Winchester Lead-Free Anvils A) Full Cartridge B) Primed Only 124
Figure 61: Winchester Lead-Free Cups A) Full Cartridge B) Primed Only 125
Figure 62: Winchester Lead-Based Anvils A) Full Cartridge B) Primed Only 126
Figure 63: Winchester Lead-Based Cups A) Full Cartridge B) Primed Only 127
Figure 64: Liberty Lead-Based Anvils A) Full Cartridge B) Primed Only 128
Figure 65: Liberty Lead-Based Cups A) Full Cartridge B) Primed Only 129

Figure 66: Federal Lead-Free Anvils A) Full Cartridge B) Primed Only 130

Figure 67: Federal Lead-Free Cups A) Full Cartridge B) Primed Only 131

Figure 68: Sellier & Bellot Lead-Free Muzzle Discharge A) Full Cartridge B) Primed Only..... 133

Figure 69: Winchester Lead-Based Muzzle Discharge A) FUll Cartridge B) Primed Only 134

LIST OF TABLES

Table 1: Summary of Ammunition Purchased 33

LIST OF ABBREVIATIONS (OR) ACRONYMS

AAS	Atomic Absorption Spectroscopy
AMPAC	Advanced Materials Processing and Analysis Center
Ar	Argon
ASTM	American Society of Testing and Materials
Au	Gold
B	Boron
Be	Beryllium
BSD	Backscattered electron detector
C	Carbon
Ca	Calcium
CA	Cluster Analysis
Cl	Chlorine
Cr	Chromium
DBX-1	Copper(I) 5-nitrotetrazolate
DDNP	Diazodinitrophenol
DPA	Diphenylamine
FET	Field Effect Transistor
FMJ	Full Metal Jacket
GC-MS	Gas Chromatography-Mass Spectrometry

GSR	Gunshot Residue
HpGeLi	High purity germanium doped with lithium
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
KDNP	Potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide
LBP	Lead-based primer
LDA	Linear Discriminant Analysis
LFP	Lead-free primer
Li	Lithium
LOD	Limit of Detection
MC	Methyl Centralite
Mg	Magnesium
MSDS	Material safety data sheet
N	Nitrogen
Na	Sodium
NAA	Neutron Activation Analysis
NC	Nitrocellulose
NCFS	National Center for Forensic Science
NG	Nitroglycerin
PC	Principal Component
PCA	Principal Component Analysis

Pd	Palladium
Pt	Platinum
SED	Secondary electron detector
SEM-EDX	Scanning electron microscope-energy dispersive x-ray
Si	Silicon
Si(Li)	Silicon doped with lithium
Sn	Tin
TGSR	Traditional gunshot residue
Ti	Titanium
TMJ	Total Metal Jacket
UCF	University of Central Florida
W	Tungsten
XRF	X-ray Fluorescence Spectrometry
ω	Fluorescence Yield

CHAPTER 1: INTRODUCTION

Gunshot residue, more commonly referred to as GSR, is residue that is left behind after the firing of a weapon and typically settles on the shooter, the victim, and that which is in the vicinity during the shooting. Typically identified by the presence of a barium (Ba), antimony (Sb), and lead (Pb) based compound present in the collected sample, it is a common method of linking a suspect to a crime. However, with the health hazards associated with traditional lead-based ammunition the use of lead-free ammunition is becoming increasingly more popular. This results in GSR which is not easily identifiable by traditional means. Although much research has been performed on the elemental and morphological composition of traditional GSR, the common method of identification via SEM-EDX is still widely used in forensics laboratories, due to the inability to characterize residue based on any other criteria. While research has been conducted on the differences between lead-based and lead-free muzzle discharge residue, few have researched other components of ammunition which may lead to other means of characterizing GSR, in the absence of the typical Ba, Sb, and Pb particles. Therefore, this research covers that gap by focusing on the priming cup present in ammunition and the residue which may originate from it, that can contribute to muzzle discharge residue.

The firing train process which occurs when a firearm is discharged consists of a series of steps and compounds, each of which play a key role in its success. The process begins in the priming cup which houses a mixture of explosives, fuels, and oxidizers. This mixture is a key component in the identification of GSR and is the origin of traditional GSR particles. Therefore,

the first goal of this research is to determine what occurs during the ignition process, more specifically what occurs within the priming cup during and after the ignition of the priming mixture. This will provide further information on where certain components of GSR originate from within the ammunition and the potential to identify these compounds in the muzzle discharge residue.

With the increasing use of lead-free alternatives to traditional lead-based priming mixtures, the common methods of identification of GSR are not always applicable. This results in the need for an alternative method of identification of GSR that allows for the identification of its lead-free counterparts. The second goal of this research is to determine the physical and chemical differences between lead-based and lead-free priming mixtures to ultimately develop a method of characterization between them.

Other components of ammunition may contribute to GSR as well, namely the cartridge case. This research also focuses on the priming cup present within the cartridge case and those metals which originate from the liquation of the priming cup. Therefore, the third goal of this research is to determine how the components of the cartridge case, more specifically the priming cup and its parts, can contribute to GSR.

With a combination of the goals thus outlined, this research seeks to determine other methods of characterizing GSR aside from the traditional methods. This will ultimately lead to the development of discrimination methods that differentiate between lead-based and lead-free priming mixtures. It is the primary objective for this research to be used in the identification of muzzle discharge residue in future research. This will benefit those working in

the field of forensics, who are experts in the area of GSR analysis, to detect the presence of GSR on a potential suspect based on more criteria, resulting in more certainty of a positive identification that GSR is present.

CHAPTER 2: LITERATURE REVIEW

2.1 Ammunition

When a firearm is discharged, a plume of residue originating from the ammunition is released from the muzzle of the weapon and may be deposited on the shooter, the target, and any objects in the vicinity during the firing. In many criminal cases, this GSR may be used to determine whether a potential suspect has fired a weapon. Ammunition is composed of many different components which aid in the proper discharge of a projectile and may contribute to the GSR left behind, including: the cartridge case, priming cup, seal, anvil, propellant, priming mixture, and the projectile itself (Figure 1).

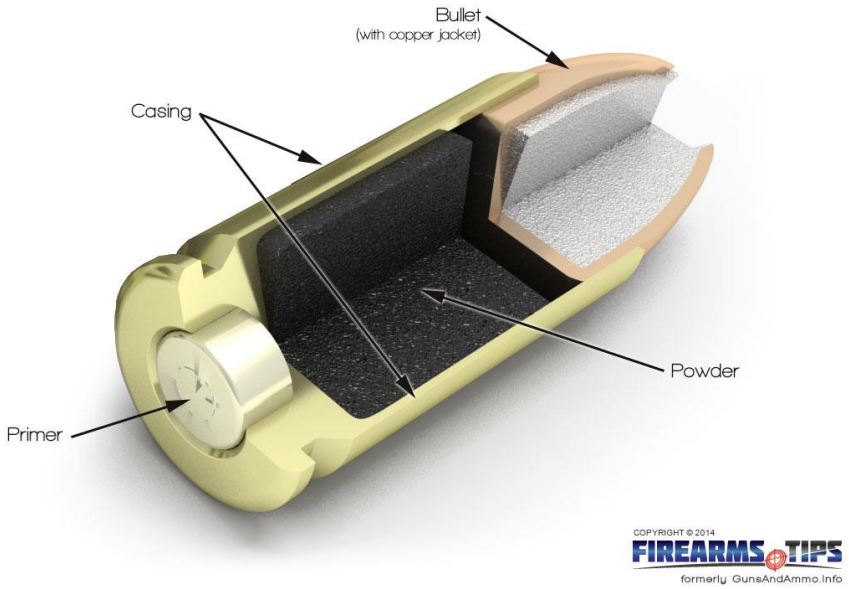


Figure 1: Schematic diagram of ammunition[1]

The cartridge case houses the various components of the ammunition (the priming cup, the propellant, and the projectile, (see Figure 1) and is designed to account for the specifications of the projectile as well as the type of ignition system (i.e. the primer), and the type of weapon used (e.g. pistol, rifle, etc.). These cartridge case parts are composed of various metallic components, the most common of which are composed of brass, typically in a 70% copper to 30% zinc ratio. However, the case may also be composed of other materials such as steel, copper, nickel plated brass, cupronickel, or aluminum, with steel being the second most common material used for ammunition cases.

The priming cup is located in the base of the cartridge case (refer to Figure 1), in what is called the primer pocket. The priming cup houses the priming mixture (i.e. the primer), the seal, and the anvil, and is typically composed of brass as used in the cartridge case. However, this may also be composed of copper, nickel plated brass, copper alloys, cupronickel, and zinc-coated steel, though these are not as common. The primer is located within the priming cup and contains a mixture of explosives, oxidizers, and fuels; traditionally lead styphnate, barium nitrate, and antimony sulfide, respectively. The priming mixture is developed to be shock sensitive and the flame that is produced allows for the ignition of the propellant. [2, 3]

Priming cups are designed in two different configurations with respect to the anvil: Berdan primers and Boxer primers (Figure 2)[4]. Berdan primers are preferred in European countries whereas the United States and Canada favor the Boxer primer as it is easier to reload.

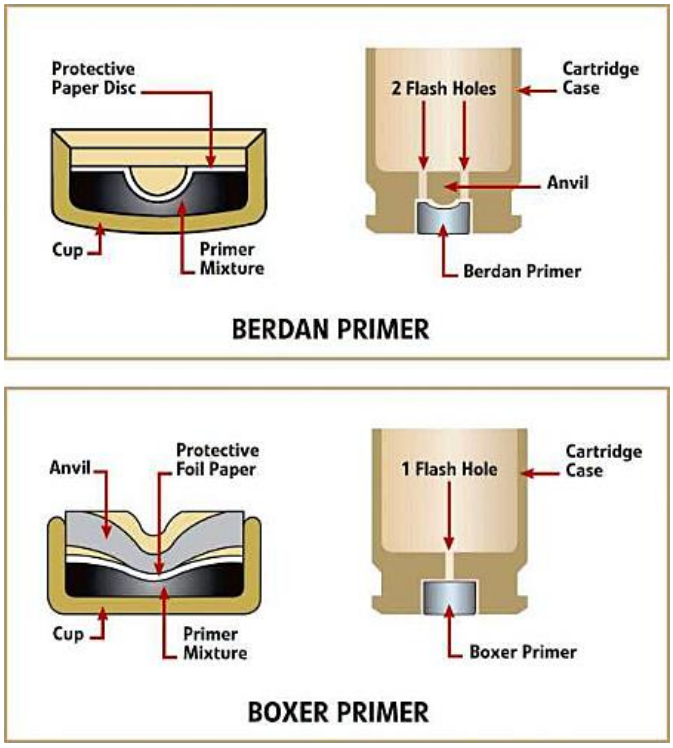


Figure 2: Primer pocket diagram[4]

The primary difference between the two types of cups is that the anvil is separated from the cup in the Boxer primer, whereas the anvil in the Berdan primer is part of the cartridge case (Figure 2).[3] The priming cup also contains a seal located between the priming mixture and the anvil which prevents the entrance of moisture into the priming mixture (see Figure 2). If moisture enters the priming cup it will prevent the explosives from effectively detonating and result in what is known as “dead” primers.[3]

The priming mixture is used to ignite the propellant, while the propellant located above the priming pocket in the cartridge case, is used for generating large amounts of pressure and gases in order to eject the projectile from the firearm. Propellants are often smokeless powders and have chemical compositions that are referred to as either single, double, or triple based.

Propellants which contain only nitrocellulose (NC) are considered single base, while those that contain NC and nitroglycerin (NG) are considered double based. The addition of a third explosive such as nitroguanidine results in a triple base propellant; however, these are typically only used in military grade ammunition rather than small arms ammunition.[3, 5]

The final component of ammunition is the projectile, which is located at the top of the cartridge case above the propellant (see Figure 1). While a projectile could be considered anything which may be expelled from a barrel, the projectiles typically encountered in small arms ammunition are bullets, pellets, or slugs, with the most common being bullets. Bullets are produced in a wide variety of shapes, sizes, and compositions depending on the purpose for which the ammunition is being used.

Although the bullet may be made from materials such as copper, brass, bronze, aluminum, steel, zinc, or tungsten, the most commonly used metal for the production of bullets is lead. The lead bullet may also be encased in a harder outer layer of a metal such as cupronickel, nickel, copper, bronze, aluminum, etc. in either a full metal jacketed (FMJ), or total metal jacketed (TMJ) fashion. FMJ indicates that the lead bullet is encased in a harder metal, however the base of the bullet is left exposed; whereas, TMJ indicates that the entire bullet is encased in the harder metal, including the base (Figure 3). [3]

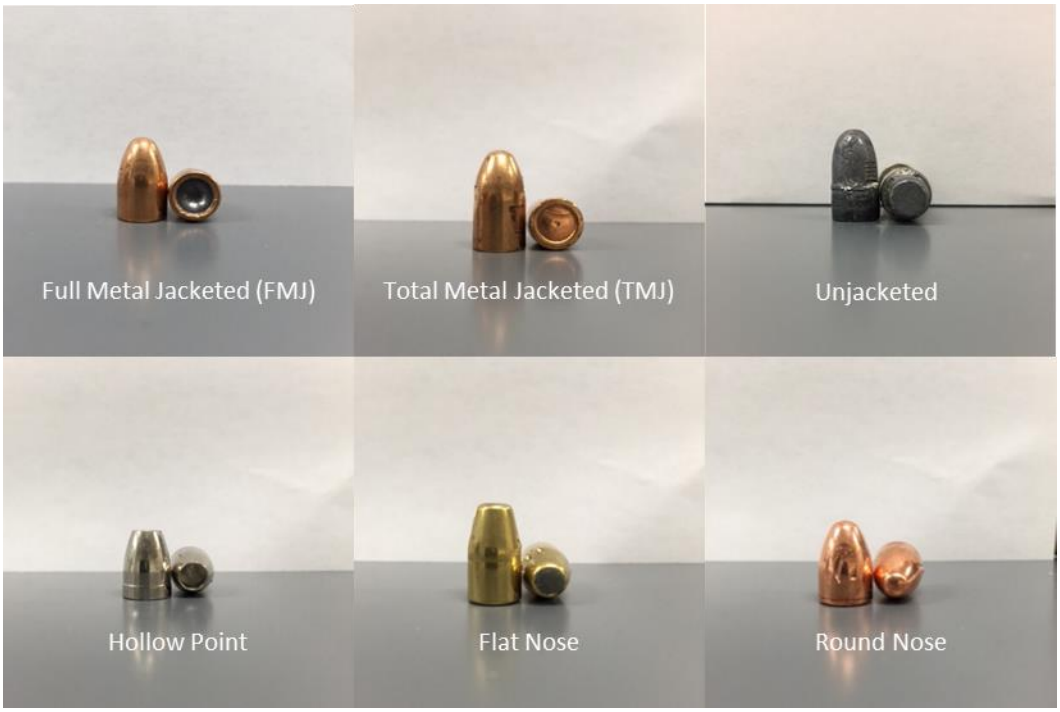


Figure 3: Designs of bullets

In summary, ammunition consists of multiple steps, all of which play an integral role in the proper discharge of a firearm. When a weapon is discharged, the firing pin hits the base of the priming cup which detonates the shock sensitive priming mixture.[2] The flame and gases produced by the priming mixture will travel through the flash hole and ignite the propellant. This results in the buildup of the gas pressure within the cartridge case and the projectile is then expelled from the barrel of the firearm. This results in a plume of GSR being released, which condenses on any objects in the vicinity due to the sudden drop in temperature and pressure upon being expelled. Additional GSR is also present in the priming cup after detonation, which originates from what is left behind after the ignition of the priming mixture.[6, 7, 8, 9]

2.2 Gunshot Residue Formation

When a firearm is discharged, the trigger is pressed releasing the firing pin which in turn strikes the base of the priming cup. The sudden force on the base of the priming cup, by the firing pin, results in the combustion of the shock sensitive priming mixture which initiates the firing train reaction.[2] Both organic and inorganic components of the priming mixture are vaporized, or liquefied, and thus the vapors and the gases created will travel through the flash hole and ignite the smokeless powder. The ignition of the smokeless powder results in the production of gases and increased pressure which expel the projectile from the barrel of the firearm.[7] As the temperature and pressure begin to decrease within the priming cup after detonation, the vaporized priming mixture components begin to condense and solidify as droplets.[9] Many of the droplets are likely to have vaporized and condensed before the smokeless powder is even ignited.[8] Residue will also exit the muzzle of the weapon, or any area which is not airtight, such as the breach. This residue consists of both the components originating from the priming mixture as well as those from the smokeless powder and will condense onto the target and any surrounding areas due to rapid cooling and the sudden drop in pressure, after ignition.[2, 6, 10]

Traditional gunshot residue (TGSR) originates from an ammunition containing a lead-based primer (LBP). Such particles are described as those which are collected from a target or from the backs of shooters hands and are often described as spheroidal in shape with a noncrystalline appearance. The particles often have a smooth surface, but may also be fuzzy, scaly, or consist of clusters of particles condensed together.[3, 8] They often range in size from 0.1

to 10µm, with some particles occasionally exceeding this magnitude and being classified as irregular in shape.[8, 10, 11, 12] Residue may also be present in the priming cup. This residue is mainly comprised of components from the priming mixture and is likely to have formed before the ignition of the smokeless powder has occurred. This typically consists of a liquefied priming mixture interspersed with condensed droplets of priming mixture.[8]

GSR consist of the gases, vapors, and particulates which originate from the ammunition within a firearm, or the firearm itself, when it is discharged. It is comprised of two primary types: organic and inorganic. Inorganic gunshot residue (IGSR) originates primarily from the priming mixture and the projectile, but may also consist of materials present in the seal, anvil, cartridge case, additives to the propellant, and the barrel of the firearm. Organic gunshot residue (OGSR) predominately originates from the propellant, but may also come from additives which could be present in the priming mixture.[3]

IGSR, from LBP, mainly consists of the metals from the fuels, oxidizers, and explosives which make up the priming mixture, as well as various additives. In traditional priming mixtures the three main components are lead styphnate which acts as the explosive, barium nitrate as the oxidizer, and antimony sulfide as the fuel. The priming mixture may also contain frictionators such as aluminum powder, sensitizers such as tetracene, and binders such as gum arabic, that may all contribute to GSR.[3, 7, 13] Priming mixtures may also contain a number of additives, which have an array of uses such as magnesium (Mg) and silicon (Si) and may also add to GSR.[7, 14] The heat of combustion liquefies the priming mixture, and the temperature of the mixture quickly exceeds the vaporization points of the Pb, Ba, and Sb present in the priming mixture resulting in

the presence of these three primary elements in GSR. Alternatively, organic GSR originates from the smokeless powders present in the ammunition, usually NC and NG, as well as components which are added to act as stabilizers, plasticizers, flash inhibitors, coolants, etc. These additives include organic materials such as diphenylamine (DPA), phthalates, graphite, powdered metals, and more.[7, 13, 14]

The presence of Pb, Ba, and Sb, originating from the LBP present in the priming cup, or a combination thereof, is often considered indicative that a weapon was fired.[3, 7, 10, 13] However, with the hazards associated with lead in lead-based ammunition, lead-free alternatives are becoming increasingly more popular leading to difficulties in analyzing lead-free GSR using traditional means.[3, 15, 16] Upon discharging of a firearm the lead originating from the lead styphnate in the priming mixture, and the lead present in the projectiles, if the projectile is unjacketed, is vaporized and released into the surrounding environment. The aerosolized lead can easily be ingested, or inhaled, and can migrate into the bloodstream, posing substantial health risks, regardless if the shooting range is indoor or outdoor.[15, 17] Lead poisoning is a serious issue and the toxicity of lead may have severe effects on many aspects of the human body. According to many researchers, lead can affect the blood, which may result in anemia. It can also affect the central nervous system, the reproductive system, and many organs in the body, such as the kidneys or the brain.[16, 18] In order to account for this problem, many ammunition manufacturers have started making lead-free priming mixtures (LFP), as well as producing lead-free bullets or encasing the lead bullets in less toxic metals. The toxic components present in the priming mixture are replaced with less toxic and more

environmentally friendly alternatives. Although lead-based primers are primarily used in ammunition, lead-free mixtures are becoming more widely used, leading to GSR which varies greatly from that of traditional lead-based ammunition.

Huynh *et al*. at the Los Alamos National Laboratory in New Mexico published criteria in 2006 that must be met for any compound replacing lead styphnate as the explosive charge in the priming mixture, namely[19, 20]:

1. Insensitivity to light;
2. Sensitivity to detonation but not too sensitive to handle and transport;
3. Thermally stable to at least 200ºC;
4. Chemically stable for extended periods;
5. Devoid of toxic metals such as lead, mercury, silver, barium, or antimony;
6. Free of perchlorate, which may be a possible teratogen and has adverse effects on thyroid function.

Replacements for lead styphnate must retain their energetic properties upon exposure to the atmosphere and must abide by the six criteria listed above.[18]

A common compound used as a primary explosive for the replacement of lead styphnate is 2-diazo-4,6-dinitro-1-phenolate, or diazodinitrophenol (DDNP). It is an environmentally friendly and energetic material, but may become darkened and unstable on exposure to sunlight.[18, 20] 1-(5-tetrazolyl)-3-guanyltetracene hydrate, or simply tetracene, is another environmentally friendly and energetic primary explosive that contains no heavy metals or perchlorate ions. This compound, however, does not meet three of the six criteria for

'green' materials due to it being sensitive to light, thermally unstable above 160ºC, and its ability to be degraded by boiling water.[18, 20] Other replacements for lead styphnate include copper(I) 5-nitrotetrazolate (DBX-1) and potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide (KDNP).[21]

In addition to the residue from the priming mixture, GSR also contains traces of partially burned and unburned smokeless powder, which is the propellant. Smokeless powders are categorized into three main classes based on the type and number of components present and can vary depending on the additives and its use. Single-based powders contain nitrocellulose (NC) as the primary explosive, which is highly flammable and often found in many consumer products. Double-based powders contain NC as well as nitroglycerin (NG) and are often used in firearm ammunition. Triple-based powders have the addition of nitroguanidine to the NC and NG for reducing muzzle flash and barrel temperatures and are typically used for military purposes.[5] Other compounds are often added in varying degrees to act as stabilizers, plasticizers, flash inhibitors, coolants, moderants, surface lubricants, gelatinizing agents, and anti-wear additives. [7, 22] As an example, diphenylamine (DPA) and methyl centralite (MC) are often added as stabilizers which act to slow down the decomposition of the NC and NG, and have often been the target of colorimetric tests derived for the identification of GSR.[5, 13]

2.3 Gunshot Residue Identification

When a sample is collected from a target or potential suspect, it is commonly analyzed via SEM-EDX in order to determine whether GSR is present and at what concentration. The

identification of the particles present in the sample is typically dependent on the chemical composition and morphology of the GSR particulates. The American Society of Testing and Materials (ASTM) has developed a protocol for the analysis of TGSR and the characteristics that should be examined upon identification of the sample.[12] For the morphology of TGSR, most of the particles detected should be spheroidal in shape and noncrystalline with a diameter between 0.5µm and 5.0µm. The remainder of the particles can be irregular in shape and ranging from 1µm up to 100+ µm. It is unusual to see particles of crystalline structure present in GSR samples, though it is not impossible. The chemical composition of the TGSR particles is comprised of the presence of Pb, Sb, and Ba, which originate from the lead styphnate, antimony sulfide, and barium nitrate, respectively.[12] The presence of these three elements along with the spherical particulates is typically considered indicative that LBP gunshot residue is present.

With the increasing use of LFPs in ammunition, GSR cannot always be analyzed based on the ASTM criteria; therefore, new research is emerging for the identification of lead-free GSR (LFGSR). A primary difference in the morphology of LBPs versus LFPs is the non-spheroidal shape of lead-free particulates. While LBP particulates can be characterized based on their spherical morphology, lead-free particles are rarely spherical and often consist of an array of shapes and sizes.[16] As described in the research by Oommen and Pierce, particles may appear as “orange peels”, “spheroids”, or “teardrops”, and in some cases they appear as spheres with “pocked”, “crackled”, or “fissured surfaces”.[17] Due to the irregularity of lead-free particulates

and the absence of Pb, Sb, and Ba, the absence of the typical GSR characteristics cannot be indicative that a weapon was not fired.

2.4 Sources of Residue Similar to Gunshot Residue

When a firearm is discharged, residue will not only escape from the muzzle of the weapon but also from other gaps and vents located in the firearm. The residue will settle on the hands, hair, and clothing of the shooter and any items within close proximity.[3] Although the residue that is thus collected from these locations may show elemental and physical characteristics of TGSR, there are other sources of TGSR-like particles which may originate from the environment or from the materials used in certain professions. The metallic characteristics of TGSR result in an elemental composition which may be similar to that of residues found in professions which utilize metal parts such as the automobile or maintenance industries.[23] Furthermore, some professions, such as the production of fireworks, may use explosives that may leave residue similar to that of the explosives used in ammunition.[24]

As stated previously, the presence of Pb, Ba, and Sb is commonly considered indicative that a firearm with a LBP ammunition was discharged. However, many professions may also result in the presence of Pb, Ba, and Sb based residue on skin or clothing. Garofano *et al*., conducted research in which samples were collected from subjects in various occupations such as plumbers, automobile electricians, car battery salesman, fireworks experts, and more, as well as materials often associated with automobiles, printing, plumbing, etc. Ultimately, it was determined that while similar in elemental composition to TGSR, the physical forms of residue

associated with such professions were easily differentiable from TGSR particles. While composed of a combination of Pb, Ba, and Sb, the particles were not consistent with the morphological characteristics considered unique to TGSR.[23]

Additional research was conducted by Torre *et al*. regarding the presence of Pb, Ba, and Sb resulting from brake linings on automobiles. This research was in agreement with Garofano *et al*. and concluded that the elemental composition is similar to that of TGSR, resulting in the need to further evaluate morphological characteristics in order to differentiate between TGSR and residue originating from environmental or occupational sources.[25]

Similar research was conducted by Mosher *et al*., in which Pb, Ba, and Sb were often considered to be present in the use of various pyrotechnic devices. Therefore, the authors investigated the similarity of firework residue compared to TGSR. The hands of firework technicians were sampled and the residue was analyzed via SEM-EDX. This research identified residue that was more similar to TGSR particles. These contained Pb and Ba, which were spheroidal in shape with a non-crystalline appearance, and a diameter within the range of typical GSR (refer to Section 2.4 Sources of Residue Similar to Gunshot Residue). While many of the particles fell above this range, they still remained within the criteria set forth by ASTM International for the analysis of TGSR.[12, 24]

2.5 Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM-EDX)

The most common method of GSR identification, and that which is laid out by ASTM International, is the use of an SEM-EDX.[12] The SEM-EDX allows for the simultaneous imaging

and elemental identification of a sample. It is a relatively nondestructive technique and allows for samples to be analyzed with very little sample preparation.[3, 7, 11, 12, 26, 27] Rather than use a beam of light, as most microscopes utilize, a SEM uses a beam of electrons to form the image of an object. It is capable of magnifying over 200 times that of an optical microscope and can magnify a sample greater than 100,000 times with relatively high resolution. Additionally, upon the electron beam striking the sample, the elements present will absorb some of the energy from the electrons and re-emit it as x-rays, which are characteristic to every element.[28] This technique is able to identify single particles both morphologically and chemically, which is useful for those criminal cases in which small amounts of GSR are present for analysis. [7]

2.5.1 Scanning Electron Microscope (SEM)

The SEM is a powerful microscope that allows for high magnification and subsequent high resolution imagery of a sample. The SEM consists of several primary components including, but not limited to: the electron gun, an anode, deflection coils, condenser lenses, an objective lens, apertures, scanning coils, and an electron detection system (Figure 4). [29, 30] The electron gun is located at the top of the column and often consists of a tungsten filament which produces a beam of electrons with energies from 1 to 30 keV. The filament is accompanied by an anode which is held at high positive potential energy. The filament is heated until the voltage difference between anode and the filament produces a beam of electrons.[29, 31]

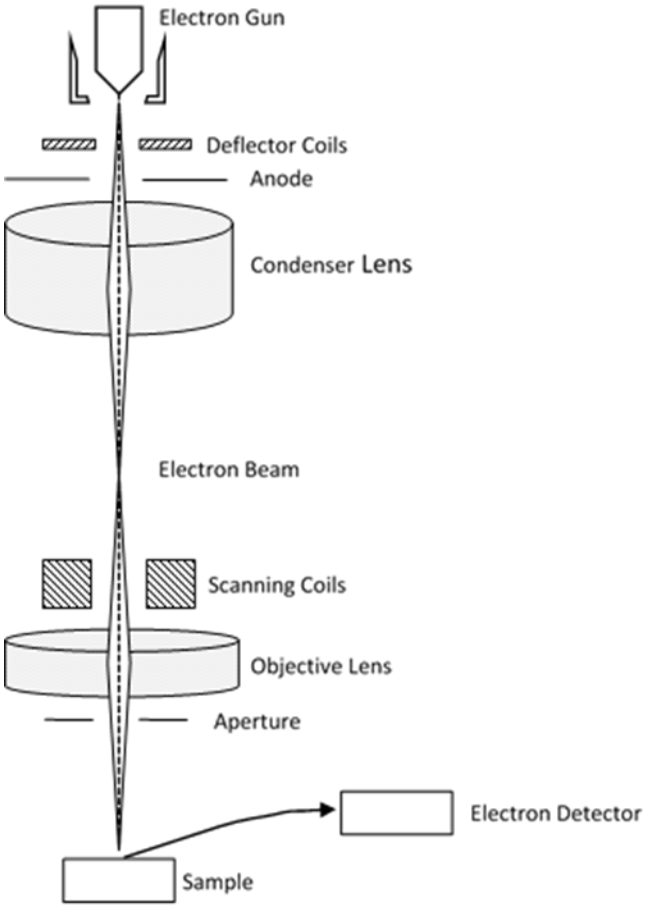


Figure 4: Schematic diagram of the scanning electron microscope

The voltage difference defines the accelerating voltage, i.e. the greater the difference in voltage the higher the accelerating voltage and the more electrons will be received by the detector.[29] Once the electron beam is produced, it is focused into a column through a series of lenses, which control for aberrations; aberrations may distort the image of the particle. A series of deflector coils at the top of the column control for misalignments in the filament which may shift during heating.[29] The first series of lenses consists of two condenser lenses that control the diameter of the beam and narrow it down to 10nm when striking the sample, with a current of

1 to 100 pA. [30, 32] Subsequently, there is an objective lens which focuses the electron beam, bringing it down to a minimal spot size (or the crossover point) on the sample. On either side of the lenses, there are apertures that remove stray electrons in order to control for aberrations in the electron beam.[29, 33]

Directly above the objective lens is the deflection system (i.e. the scanning coils), which rasters the beam across the sample. This system consists of a series of magnetic coils, one of which controls the *x* direction, while a second coil controls for the *y* direction. This manipulates the direction of the electrons as they enter the objective lens before finally striking the sample.[29, 31, 33] In order to acquire an image of a larger area of the sample the electron beam is rastered across a larger area. Similarly, to magnify the sample the beam is rastered across a smaller area. Additionally, since electrons are charged particles, they can often interact with air molecules and, if operated under ambient conditions, the beam filament can be damaged. To avoid this, this entire process is operated under an extremely high vacuum.[32]

Once the electron beam reaches the specimen, electron signals are generated from the beam/specimen interactions. When the beam and the sample interact, electrons are scattered from different depths of the sample, roughly 10 nm for secondary electrons and 5 µm for backscattered electrons.[29] These electrons escape from the surface and are able to be detected by either a secondary electron detector (SED) or backscattered electron detector (BSD), which are attached to the SEM. [30] There are two different types of scattering that occur when an electron interacts with a sample, elastic and inelastic. Elastic scattering occurs when an electron strikes the electrical field of the nucleus of an atom and rebounds with a slight angular

deflection but little to no loss in energy.[29, 31, 34] The mass of the nucleus is much larger than the mass of the electron interacting with it, which prevents any transfer of energy.[29] Backscattered electrons, which are higher in energy (>50eV), result from the escape of electrons from deeper within the sample and result from elastic collisions.[3, 29, 30, 31, 32, 33, 34] Alternatively, inelastic scattering occurs when the beam electron strikes the electrical field of the electrons present in the sample, transferring energy to the atom and causing the release of a secondary electron.[29, 31] Secondary electrons, which are lower in energy (<50eV), result from the escape of electrons close to the samples surface and result from inelastic collisions. In order for the SEM to create an image, elastically or inelastically deflected electrons are detected by either a BSD or SED, respectively. SED is the primary method of obtaining SEM images, as most electrons emitted from a specimen have a relatively low energy (<50eV).[3, 32, 33]

2.5.2 Energy Dispersive X-ray Spectrometer (EDX)

While the SEM is useful for the high resolution imaging of GSR samples as well as other forensic disciplines, forensic analysts typically utilize the elemental composition in conjunction with the physical characteristics for the identification of samples. Therefore, the SEM is often coupled with an energy dispersive x-ray spectrometer (EDX), which allows for the elemental analysis of a sample. The ejection of an x-ray from the target atom can be better understood by looking at the Bohr model of the atom (Figure 5). Electron shells are designated K, L, M, N, and O, with the K shell being closest to the nucleus which houses electrons that are more tightly bound to the atom than the subsequent shells. K shell electrons are the most stable because

they have the lowest amount of energy, and thus require the highest amount of energy to be expelled from the atom.[29, 31, 33, 34, 35]

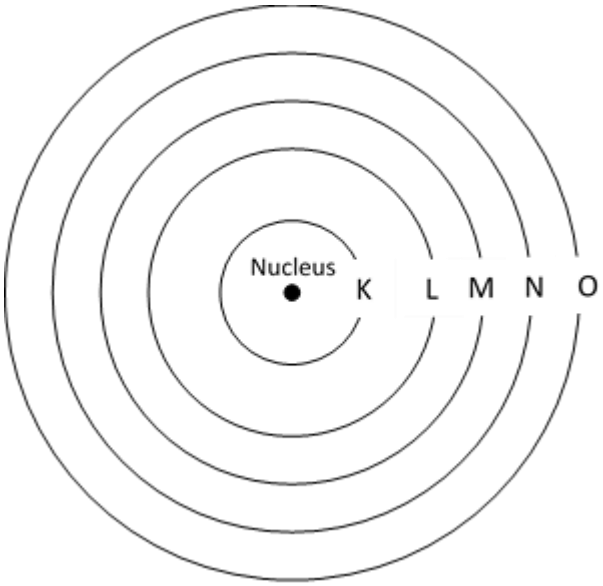


Figure 5: Bohr model of the atom

When the electron beam strikes the sample, those electrons closest to the nucleus of the target atoms (i.e. the K shell electrons) are excited to higher energy levels, subsequently causing the higher energy level electrons (i.e. the L shell electrons) to drop to lower energy levels to fill the vacancies. The excess energy generated from the difference between the higher energy level and the lower energy level can be emitted as x-rays, known as K-line x-rays. [3, 29, 31, 32, 34, 35] Additionally, other energy levels may be subject to energy transitions as well, resulting in gaps in different shells. For example, if an L shell electron is excited to a higher energy level, the resultant x-ray would be known as an L line. Thus, these energy sequences generated are characteristic to each element.[35] However, lower atomic number elements have a smaller

probability of producing x-rays, aka the fluorescence yield (ω), and a low energy associated with x-rays which are able to be released. Thus, an EDX is only able to detect those elements above an atomic number of 4, i.e. atoms heavier than boron (B).[30]

An EDX consists of three primary components, including: an x-ray detector, pulse processor, and analyzer. The x-ray detector is comprised of a collimator assembly, electron trap, window, crystal, field effect transistor (FET), and a cryostat, which houses the liquid nitrogen needed for cooling (Figure 6). All of the components of an EDX work in unison to detect and analyze the elemental composition of a sample.

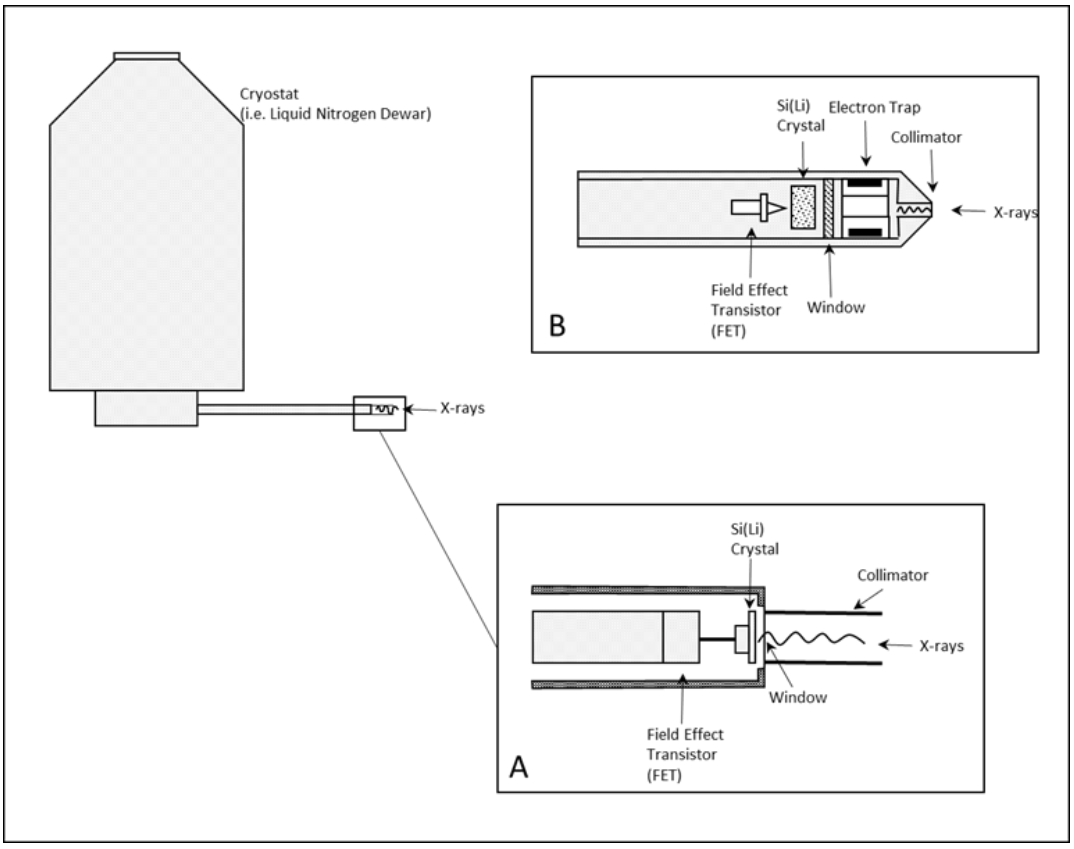


Figure 6: A) A schematic showing the general set-up of an EDX detector. B) The schematic of the detector used in this project

The first component of the detector, the collimator assembly, is designed to allow only those x-rays that originate from the area being excited by the electron beam to pass through to the detector. The collimator assembly consists of a hollow metal tube placed outside the detector, which is directed at the specimen so only those x-rays originating from the sample travel up the center. This ensures that x-rays which may originate from other areas in the chamber are not detected. The electron trap is located adjacent to the collimator assembly and is composed of magnets designed to repel any stray electrons, which may cause harm to the detector and prevents them from entering the chamber.[29, 36] Following the electron trap is the window which must be thick enough to act as a barrier to control the vacuum in the detector while not so thick as to prevent the passage of lower energy x-rays. This window is typically one of three types, namely: beryllium (Be), thin organic polymers, or windowless. Beryllium may be rolled into a thin sheet in order to act as a window for the detector, however, the strength of the sheet is at the expense of its ability to transmit x-rays. The thinner the Be sheet, the more x-rays can be transmitted through it but the weaker it is in terms of holding the necessary vacuum for the detectors. This results in a window which absorbs lower energy x-rays, allowing only elements greater than sodium (Na) to be detected. An organic polymer such as Mylar (i.e. polyethylene terephthalate) is another configuration of window which is much thinner than the Be window and allows lower energy x-rays to pass through while maintaining a strong window.[29, 32, 36] Because polymer-based windows are able to allow the passage of lower energy x-rays and therefore allow the detection of lighter elements, they are becoming more common in detectors.[36] Windowless detectors are a much less common because they utilize a Be

window that may be moved out of the way once the chamber has reached a high vacuum. While this allows for the passage of much lower energy x-rays, it also results in a layer of contamination from gases which may be formed in the chamber and may absorb some of the x-rays.[29]

Following the window is a semiconductor crystal, which converts the incoming x-rays into a unit that can be easily measured, i.e. an electric charge. A reverse bias (i.e. negative-positive bias) is placed on opposite sides of the crystal creating a "depletion zone," which separates the holes and electrons, inhibiting the flow of electrical current. When an x-ray enters the detector, an electron-hole pair is created which reappears as a charge on the other side of the diode, and thus a current is produced. The current produced allows for the measurement of X-ray energies, which are characteristic to each element.[29, 31] The crystal is typically composed of either silicon doped with lithium (Si(Li)) or high purity germanium doped with lithium (HpGeLi). Si(Li) are more commonly used, as lithium is relatively immobile in silicon crystals when at room temperature whereas lithium is more mobile at room temperature in germanium crystals, resulting in the lithium drifting out of the crystal over time. Additionally, Si(Li) crystals have greater analytical sensitivity and can be warmed to room temperature without damaging the crystal. [29, 36] Once the x-rays have been converted into an electric current, the charge can be measured by a FET, which then converts the current into a voltage. The FET is located directly behind the detector to minimize noise which may be produced by it and amplifies the week signal produced by the detector. [29] The final component of the EDX detector consists of a

cryostat filled with liquid nitrogen, which cools both the crystal and the FET to reduce electronic noise as well as prevent the mobilization of the lithium within the crystal.[29, 31, 32, 36]

In summary, an electron beams strikes the sample which excites lower energy electrons to higher energy levels and forces higher energy level electrons to fall to lower energy levels to fill the vacancies. Upon the movement of an electron from a higher energy level to a lower energy level, an x-ray is released which travels to the detector. When the x-ray reaches the detector it strikes the crystal which converts it into an electric charge that is then converted into a voltage by the FET. These x-ray frequencies generated are characteristic to each element.[30, 32, 36]

2.6 Other Laboratory Testing

Other analytical methods have been utilized for the identification of GSR, as well, however, they are less common in typical forensics laboratories. Neutron activation analysis (NAA), which is based on atoms of elements absorbing neutrons when submitted to radiation by a nuclear reactor, was used in the 1960s due to its ability to quantify barium and antimony. However, due to the risks associated with requiring a readily available nuclear reactor, high equipment costs, and poor limit of detection, the methodology has since been replaced by other techniques. [3, 26]

Atomic absorption spectroscopy (AAS) has been determined to be a suitable method for the identification of certain elements present in GSR; however, this method is not able to perform multielement analysis and thus proves to be at a disadvantage to currently used

techniques. Other methods of GSR detection that have been used include x-ray fluorescence spectrometry (XRF) and inductively coupled plasma mass spectrometry (ICP-MS), as well as high-performance liquid chromatrography (HPLC) and gas chromatography coupled to mass spectrometry (GC/MS) for the detection of organic residues. [3, 26]

2.7 Field Tests

Testing for GSR can be performed both in the field, as a presumptive test, and more conclusively in the laboratory. Field tests typically consist of a colorimetric test used for the determination of the primary metals present in ammunition, but the samples must then be further analyzed in a laboratory. The most common colorimetric tests used for the detection of GSR are diphenylamine (DPA) and sodium rhodizonate. DPA, when made into a solution with concentrated sulfuric acid, will have a blue response when it interacts with nitrates, such as those left behind from the NG and NC in the smokeless powder.[7, 37]

The DPA test is useful for the organic components of GSR, whereas the sodium rhodizonate test is useful for the metallic components, more specifically two of the primary components of traditional priming mixtures, Pb and Ba. When dissolved in water, the orange solution will turn Pb and Ba particles red-brown. Due to the similarity in color between the solution and the color change, this reaction is often difficult see and interpret.[37]

Colorimetric testing for GSR is not often encountered in the field due to the presumptive nature of the tests. Although the tests will detect the presence of specific

compounds or elements, they are not indicative of GSR and, therefore, further testing must be performed in the laboratory for confirmation.[7]

2.8 Sample Preparation

2.8.1 Sample Collection

The primary method of GSR collection from a crime scene or the backs of shooters hands is using an aluminum stub (Figure 7A) covered with a conductive adhesive material. During SEM-EDX analysis, the conductive adhesive material allows for a current of electrons to be generated within the sample, rather than the electrons building up on the adhesive surface itself.[29] The adhesive is typically composed of carbon, which gives it a black coloration and allows for the conductivity of electrons in the SEM (Figure 7B). Clear adhesive tape may also be used to collect GSR but would require the addition of a carbon coating to reduce electron buildup. Another less common method of GSR collection is the use of liquid adhesives, which typically consist of colloidal graphite (Figure 7C).[2, 38] According to Reid *et al*., the liquid method of adhesion shows very few adhesive qualities, and is a less practical method for utilization in field as it must be applied to the aluminum stub directly before sampling. Should the liquid be applied to the stub too soon, it becomes nonadhesive if allowed to dry before sampling. [38] Another method of sample collection, though a less common one, involves the use of a cotton swab moistened with alcohol. Research suggests that the carbon based adhesive stub is a more practical and effective method of GSR collection, as it allows for the quick and easy collection of particulates and requires minimal sample preparation for use in the SEM-EDX. [38]

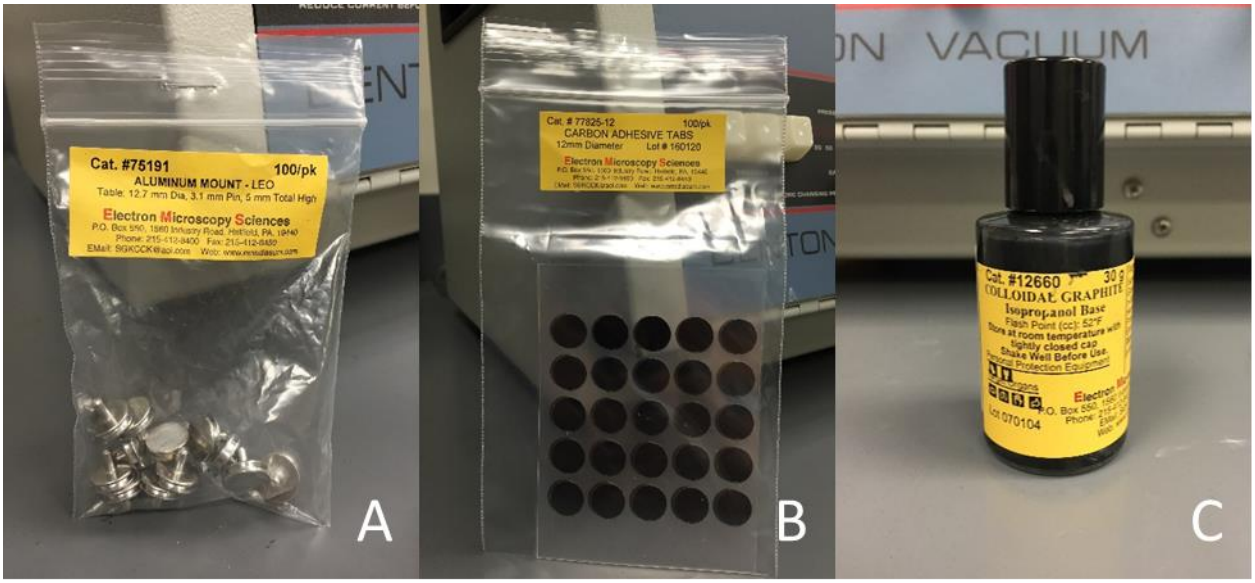


Figure 7: A) Aluminum scanning electron microscope mounts B) Carbon adhesive tabs C) Liquid adhesive composed of colloidal graphite in an isopropanol base

While the carbon adhesive is ideal for the collection of muzzle discharge particles, it does not hold cartridge case parts. The liquid adhesive, though ineffective in collecting GSR particulates directly from crime scenes, is useful for the adherence of cartridge case parts to aluminum stubs for SEM-EDX analysis. There are several benefits to using the liquid adhesive, it 1) allows for the sample to be placed strategically around the aluminum stub while leaving designated areas of the stub clear for sample numbering or labeling, 2) provides a conductive material to reduce electron buildup during SEM analysis, 3) allows for the sample to be leveled, and 4) has no negative effects on the elemental identification of the sample (see Figure 8).

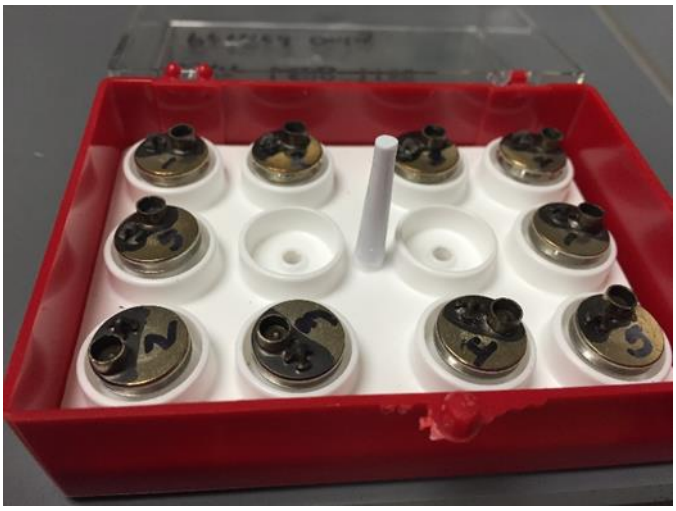


Figure 8: Example of samples prepared for SEM-EDX analysis

2.8.2 Sample Coating

In a SEM, the conductive nature of the sample is important because it allows for the flow of electrons through the sample to generate an image. If the material is non-conductive, then, when it is bombarded with electrons, a layer of electrons buildup on the insulating sample; the buildup of electrons is known as charging. Charging results when the sample is irradiated with the electron beam, and the electrons are unable to flow through sample, resulting in bright areas on the and sample making it difficult to view in the SEM. [27, 30] A way to reduce the potential of charging is by coating the sample with a more conductive material or metal such as gold-palladium (Au/Pd), tungsten (W), chromium (Cr), platinum (Pt), titanium (Ti), or carbon (C).[32] When choosing a material for coating the sample, the x-ray signals from the coating material, should be considered. If EDX is required for analysis, the x-ray spectra will show peaks from the coating material which may interfere with the target peaks from the specimen. A common method to avoid this interference is by coating the sample with carbon,

which results in an almost undetectable signal, or a signal that will typically not interfere with most major elements.[27, 29, 31] This is based on the fact that the x-ray signal generated from carbon has a low enough energy that it will appear to the far left of the spectra, rather than overlapping with the higher energies of the target elements (see Figure 9).

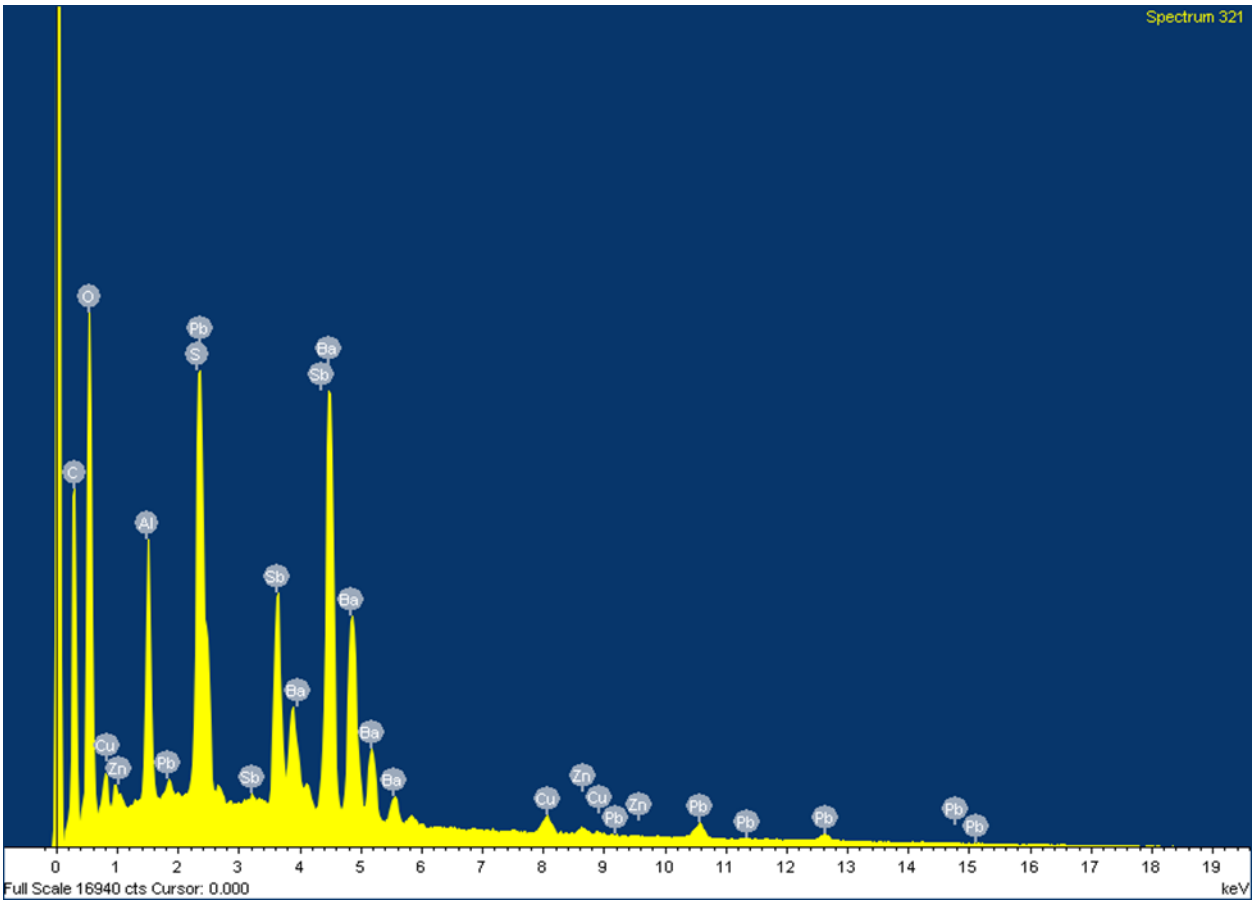


Figure 9: EDS Spectra for a particle from the Federal Lead based ammunition. The carbon peak appears to the far left of the spectra rather than overlapping with the key elements, i.e. Pb, Ba, and Sb.

The two primary techniques utilized when coating a sample are thermal evaporation and sputter coating. Thermal evaporation is used when carbon is the desired coating material and involves the evaporation of the carbon onto the sample. The sample is placed in a vacuum sealed chamber with a filament on which carbon yarn is wound (Figure 10). The filament is heated which, in turn heats, the carbon yarn until the vaporization temperature of the yarn is reached. Subsequently, carbon atoms will vaporize and coat the sample, which is placed directly in its line of sight. [27, 29, 31]

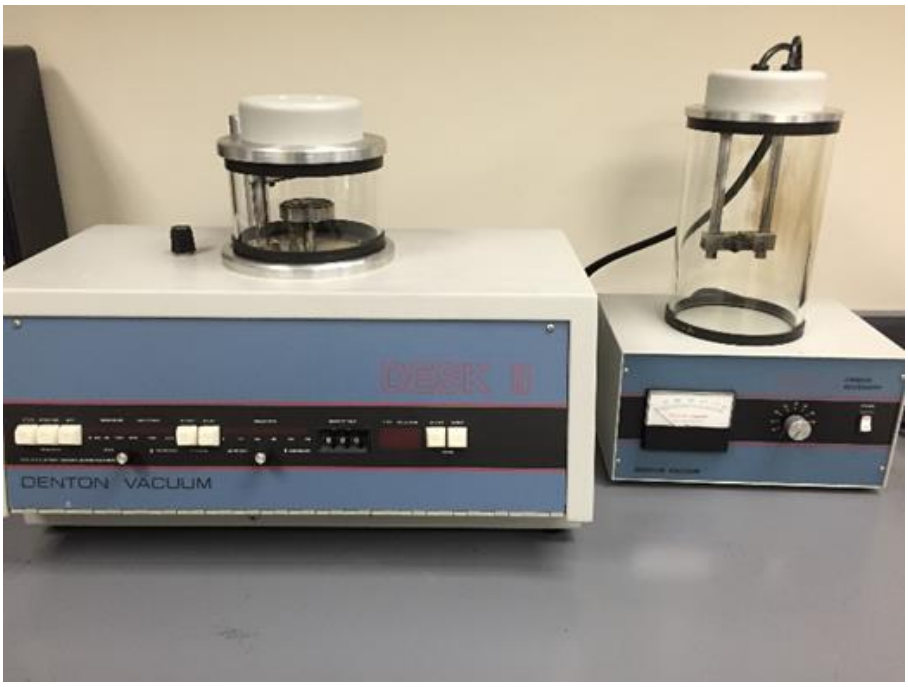


Figure 10: Pictured above is the Denton Sputter/Coater. The instrument to the left is used for the sputter/coating of Au/Pd, while the instrument to the right is the additional carbon accessory for thermal evaporation.

A second method uses a sputter coating technique, which involves the erosion of atoms from the target coating material. This technique works by placing the sample in a vacuum sealed chamber and introducing an inert gas such as argon (Ar) or Nitrogen (N) to the chamber (Figure 10). This ensures that the chamber is free of residual gases and creates an atmosphere composed solely of Ar (or N). The sputter-coater is set up as a diode, where it contains two electrodes, an anode (the sample), and a cathode (the Au/Pd). The argon atoms present in the chamber will be induced to ions by losing an electron, which will collide with the Au/Pd cathode and release metal atoms. Thus, the metal atoms will diffuse and settle on the sample. This provides a relatively even coating of a conductive material but results in the presence of Au and Pd peaks in the EDX spectra, which may interfere with target elements. Consequently, this method is typically utilized when only imaging is desired.[27, 29, 31]

CHAPTER 3: METHODS

3.1 Samples

Lead-based and lead-free 9mm ammunitions from four different manufacturers were purchased from online suppliers (Table 1). Fifty rounds of each Winchester, Sellier & Bellot, and Federal, and sixty rounds of the Liberty were purchased. These ammunitions were selected due to the availability of both a lead-based and lead-free ammunition from the same manufacturer.

Table 1: Summary of Ammunition Purchased

Manufacturer	Primer Composition	Grain	Projectile	Priming cup	Abbreviation	Instrument
Federal	LBP	115	FMJ	Ni Plated	FedLB	Full: NCFS Primed: NCFS
Federal	LFP	147	TMJ	Ni Plated	FedLF	Full: NCFS Primed: AMPAC
Liberty	LBP	50	Hollow Point	Brass	LibLB	Full: NCFS Primed: NCFS
Liberty	LFP	50	Hollow Point	Ni Plated	LibLF	Full: NCFS Primed: NCFS
Winchester	LBP	115	FMJ	Brass	WinLB	Full: NCFS Primed: NCFS
Winchester	LFP	147	Flat Nose Brass Enclosed Base	Ni Plated	WinLF	Full: NCFS Primed: NCFS
Sellier & Bellot	LBP	115	FMJ	Brass	S&BLB	Full: AMPAC Primed: NCFS
Sellier & Bellot	LFP	115	TMJ	Ni Plated	S&BLF	Full: NCFS Primed: AMPAC

3.2 Sample Preparation

Twenty-five rounds of each Sellier & Bellot, Winchester, and Federal, and thirty rounds of Liberty were disassembled using a clamp and pliers to remove the projectile from the cartridge case and subsequently the smokeless powder, leaving only the priming cup assembly (i.e. primed only cartridges). The remaining cartridges were left intact with the projectile, smokeless powder, and priming cup assembly (i.e. full cartridges). With the assistance of the University of Central Florida Police Department, both the full cartridges and the primed only cartridges were fired with a 9mm Glock, which was cleaned between the firing of each ammunition using a Remington 40-X bore cleaner and Outer's cotton patches. The ammunition was fired down range and the fired cartridge cases subsequently collected.

The collected fired cartridge cases were returned to the lab and the priming cup was removed from the cartridge case using either a Lee Reloading Press or Harvey Depriming tool depending on the diameter of the flash hole (Figure 11). Once the cartridges were deprimed, the anvil was removed from the priming cup assembly and the priming cup and anvil were prepared for SEM-EDX analysis. For each type of ammunition (both the full and primed only cartridges), five cups and their respective anvils were chosen and adhered to aluminum SEM stubs via colloidal graphite. The graphite was allowed to dry, and the stub was then coated with carbon using a Denton Vacuum Sputter/Coater (Moorestown, NJ) with carbon yarn via the sputter coating method (refer to Section 2.8.2 Sample Coating, Figure 10). The priming cups and anvils were then directly analyzed using the SEM-EDX.

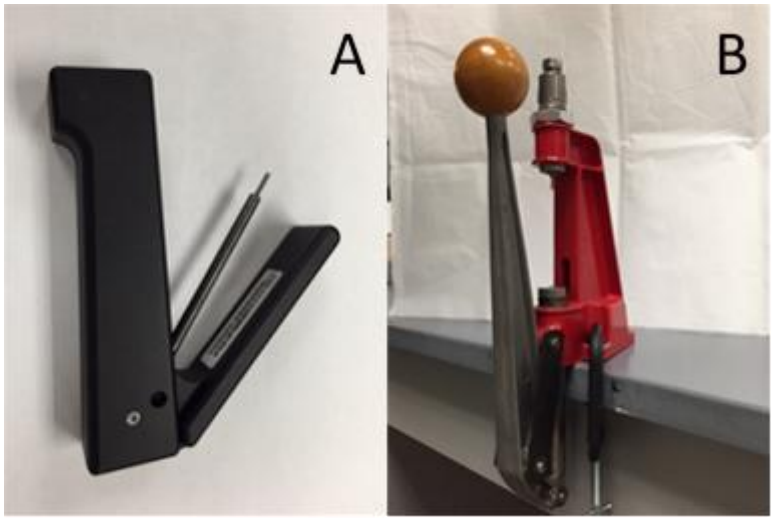


Figure 11: A) Harvey Depriming tool used for most of the cartridge cases B) Lee Reloading Press using for those cartridge cases which had a small flash hole

3.3 SEM-EDX Analysis

Most samples were analyzed using a LEO 1450VP SEM coupled with Oxford Energy Dispersive Microanalysis Hardware located at the National Center for Forensic Science (NCFS) in Orlando, FL (see Figure 12A). However, when the primary system went down, several samples were analyzed at the UCF Advanced Materials Processing and Analysis Center (AMPAC) in Orlando, FL using a JEOL JSM-640LV SEM coupled with an EDAX Gensis 700 EDS Software (see Figure 12B and Table 1). The samples were scanned using a secondary electron detector at a magnification ranging from 200 to 500x, an accelerating voltage of 20 keV and a working distance of 10mm. The spot size was set at approximately 400 which was increased accordingly to adjust for the difference in dead time per sample. The beam current was kept constant at 100μA.

Figure 12: A) LEO 1450 VP SEM located at NCFS B) JEOL JSM-640LV SEM located at AMPAC

The GSR particles were scanned manually and analyzed based on two criteria, the shape of the particle and the location in the base of the priming cup or on the anvil. For lead-based ammunition, spherical particles were the priority to analyze, and when spherical particles were not present, particles of an irregular shape were chosen instead. For lead-free ammunition, spherical particles were typically unlikely and, thus, particles were chosen based on their smooth structure. The second criteria involved the optimal position of the particles in the base of the priming cup or on the legs of the anvil. Due to the high walls of the priming cups, it was more difficult to generate a spectra of the particles located on the side nearest the detector. Unfortunately, stubs could not be turned in the instrument to get a better view. Therefore, particles were chosen on the side of the priming cup furthest from the detector in order to

allow the detector a better chance of gathering x-rays. For the anvils, particles located on the far side of the anvil from the detector were often blocked by the apex of the anvil and, thus, particles located nearest the detector were chosen for analysis. Particles 10-20µm in size were chosen for analysis as particles too small in diameter would result in the beam going straight through to the surface underneath. An analysis time of 400s was determined to be sufficient per sample in order to collect sufficient x-rays to develop a proper EDX spectra. For each type ammunition, for both the full and primed only cartridges, five anvils and five cups were chosen for analysis. Each priming cup and anvil was analyzed three times, allowing for a collection of thirty total spectra for each cartridge type.

3.4 Muzzle Discharge

In addition to the cartridge cases, two muzzle discharge samples were collected as a comparison to the priming cup residue. This will bridge the gap between the residue typically collected at crime scenes and the origin of it within the cartridge case. Both the full and primed only cartridges were fired at cotton targets and the residue was collected using aluminum stubs with carbon adhesive tabs (refer to Figure 7). The samples were then coated with carbon and analyzed via the SEM-EDX. A spectra was collected for three separate particles, as well as one spectra for the entirety of the stub.

CHAPTER 4: STATISTICAL ANALYSIS

4.1 Data Normalization

For each ammunition, the primed only and the full cartridges, both images and spectra were acquired and exported to Microsoft Word®, and Text® or Excel® files. An image at the lowest possible magnification was collected to show an overview of the cup and anvil and subsequent images were taken to show where the spectra was collected on the sample. Data was collected in triplicate per priming cup and anvil and the resultant spectra were exported in both Word and Text or Excel files. The raw data from the Text or Excel files were condensed into one Excel workbook per type of ammunition to give a total of eight workbooks. Each workbook contained two sheets, one for the full cartridges and one for the primed only cartridges. Each worksheet then contained the raw data for the thirty total spectra collected for each type of ammunition. Once all of the raw data was condensed, the three spectra for each cup, or anvil, were then averaged and the averaged data was placed in another worksheet, resulting in four worksheets per workbook (Figure 13).

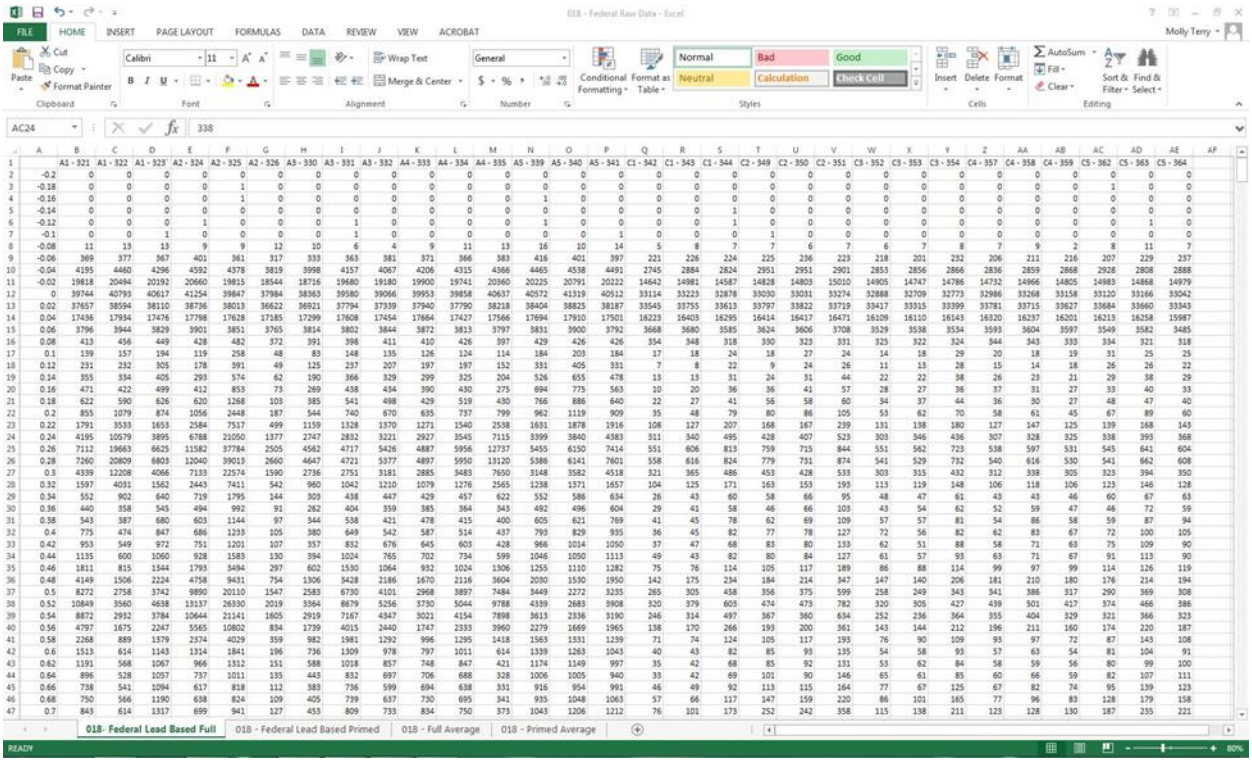
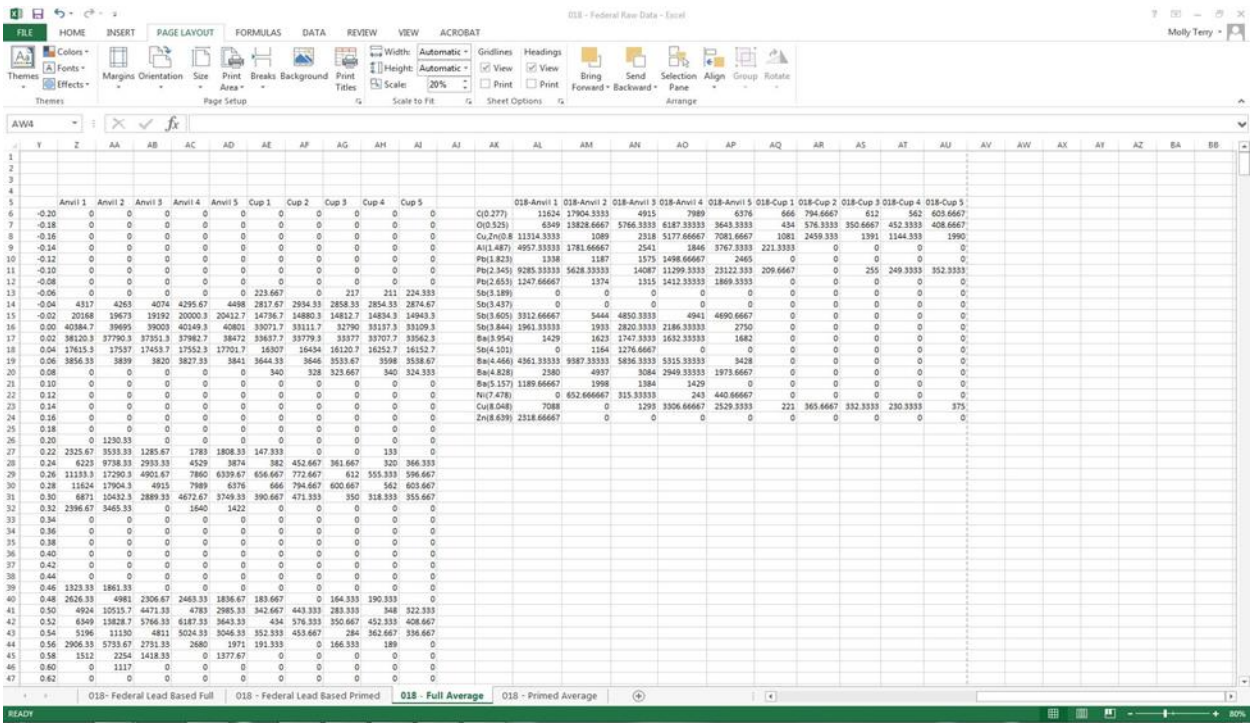


Figure 13: Raw spectral data condensed into one workbook per ammunition. This workbook corresponds to the Federal Lead-based ammunition. The letter in each column header designates the anvil or cup number while the number indicates the spectra number

Once the spectral data was averaged only those peaks which were three times the baseline were determined to be significant. An average was taken of a portion of the baseline of the spectra, which was multiplied by three to determine the minimum signal intensity (i.e. limit of detection (LOD)) required to be considered significant. The spectral data was then processed to leave only the intensities of the significant signal peaks while changing all other intensities to zero. Due to the inconsistencies in GSR and analytical instruments, the significant peaks were then picked out based on their correlation to certain elements. To be precise, each element has an energy associated with it and peaks could be picked out based on the energy they appear at (Figure 14). The specified elemental peak intensities were then condensed

among all of the ammunitions into two additional workbooks. One workbook contained one dataset for all of the peak intensities associated with the anvils for the full cartridge ammunition, while the second dataset contained the peak intensities for the cups for the full cartridge ammunition. A second workbook was created in the same manner for the primed only cartridges. Once all of the peak picked spectral data was condensed, the entirety of the data was processed using the unit vector normalization procedure. That is, all of the peak intensities were divided by the square root of the sum of squares of all included intensities (Equation 1).[39]



	Anvil 1	Anvil 2	Anvil 3	Anvil 4	Anvil 5	Cup 1	Cup 2	Cup 3	Cup 4	Cup 5
-0.20	0	0	0	0	0	0	0	0	0	0
-0.18	0	0	0	0	0	0	0	0	0	0
-0.16	0	0	0	0	0	0	0	0	0	0
-0.14	0	0	0	0	0	0	0	0	0	0
-0.12	0	0	0	0	0	0	0	0	0	0
-0.10	0	0	0	0	0	0	0	0	0	0
-0.08	0	0	0	0	0	0	0	0	0	0
-0.06	0	0	0	0	0	223.667	0	217	211	224.333
-0.04	4317	4263	4074	4295.67	4498	2817.67	2934.33	2858.33	2854.33	2874.67
-0.02	20168	19673	19192	20000.3	20412.7	14736.7	14880.3	14812.7	14834.3	14943.3
0.00	40384.7	39695	39003	40149.3	40801	39071.7	33111.7	32790	33137.3	33109.3
0.02	38120.3	37790.3	37351.3	37982.7	38472	33637.7	33779.3	33377	33707.7	33562.3
0.04	17615.3	17537	17453.7	17552.3	17701.7	16307	16434	16120.7	16252.7	16152.7
0.06	3856.33	3839	3820	3827.33	3841	3644.33	3646	3533.67	3598	3538.67
0.08	0	0	0	0	0	0	340	328	323.667	340	324.333
0.10	0	0	0	0	0	0	0	0	0	0	0
0.12	0	0	0	0	0	0	0	0	0	0	0
0.14	0	0	0	0	0	0	0	0	0	0	0
0.16	0	0	0	0	0	0	0	0	0	0	0
0.18	0	0	0	0	0	0	0	0	0	0	0
0.20	0	1230.33	0	0	0	0	0	0	0	0	0
0.22	2325.67	3533.33	1285.67	1783	1808.33	147.333	0	0	133	0
0.24	6223	9738.33	2933.33	4529	3874	382	452.667	361.667	320	366.333
0.26	11133.3	17290.3	4901.67	7860	6339.67	656.667	772.667	612	555.333	596.667
0.28	11624	17904.3	4915	7989	6376	666	794.667	600.667	562	603.667
0.30	6871	10432.3	2889.33	4672.67	3749.33	390.667	471.333	350	318.333	355.667
0.32	2396.67	3465.33	0	1640	1422	0	0	0	0	0
0.34	0	0	0	0	0	0	0	0	0	0
0.36	0	0	0	0	0	0	0	0	0	0
0.38	0	0	0	0	0	0	0	0	0	0
0.40	0	0	0	0	0	0	0	0	0	0
0.42	0	0	0	0	0	0	0	0	0	0
0.44	0	0	0	0	0	0	0	0	0	0
0.46	1323.33	1861.33	0	0	0	0	0	0	0	0
0.48	2626.33	4981	2306.67	2463.33	1836.67	183.667	0	164.333	190.333	0
0.50	4924	10515.7	4471.33	4783	2985.33	342.667	443.333	283.333	348	322.333
0.52	6349	13828.7	5766.33	6187.33	3643.33	434	576.333	350.667	452.333	408.667
0.54	5196	11130	4811	5024.33	3046.33	352.333	453.667	284	362.667	336.667
0.56	2906.33	5733.67	2731.33	2680	1971	191.333	0	166.333	189	0
0.58	1512	2254	1418.33	0	1377.67	0	0	0	0	0
0.60	0	1117	0	0	0	0	0	0	0	0
0.62	0	0	0	0	0	0	0	0	0	0

	018-Anvil 1	018-Anvil 2	018-Anvil 3	018-Anvil 4	018-Anvil 5	018-Cup 1	018-Cup 2	018-Cup 3	018-Cup 4	018-Cup 5
C(0.277)	11624	17904.3333	4915	7989	6376	666	794.6667	612	562	603.6667
O(0.525)	6349	13828.6667	5766.3333	6187.33333	3643.3333	434	576.3333	350.6667	452.3333	408.6667
Cu,Zn(0.8	11314.3333	1089	2318	5177.66667	7081.6667	1081	2459.333	1391	1144.333	1990
Al(1.487)	4957.33333	1781.66667	2541	1846	3767.3333	221.3333	0	0	0	0
Pb(1.823)	1338	1187	1575	1498.66667	2465	0	0	0	0	0
Pb(2.345)	9285.33333	5628.33333	14087	11299.3333	23122.333	209.6667	0	255	249.3333	352.3333
Pb(2.651)	1247.66667	1374	1315	1412.33333	1869.3333	0	0	0	0	0
Sb(3.189)	0	0	0	0	0	0	0	0	0	0
Sb(3.437)	0	0	0	0	0	0	0	0	0	0
Sb(3.605)	3312.66667	5444	4850.3333	4941	4690.6667	0	0	0	0	0
Sb(3.844)	1961.33333	1933	2820.3333	2186.33333	2750	0	0	0	0	0
Ba(3.954)	1429	1623	1747.3333	1632.33333	1682	0	0	0	0	0
Sb(4.101)	0	1164	1276.6667	0	0	0	0	0	0	0
Ba(4.466)	4361.33333	9387.33333	5836.3333	5315.33333	3428	0	0	0	0	0
Ba(4.828)	2380	4937	3084	2949.33333	1973.6667	0	0	0	0	0
Ba(5.157)	1189.66667	1998	1384	1429	0	0	0	0	0	0
Ni(7.478)	0	652.666667	315.33333	243	440.66667	0	0	0	0	0
Cu(8.048)	7088	0	1293	3306.66667	2529.3333	221	365.6667	332.3333	230.3333	375
Zn(8.639)	2318.66667	0	0	0	0	0	0	0	0	0

Figure 14: This shows the raw spectral data once it has been peak picked. The data on the left shows the intensities for the significant signals. The data on the right shows the data peak picked based on its correlation to specific elements.

$$\frac{x_i}{\sqrt{\sum_{i=1}(x_i)^2}} \quad (1)$$

4.2 Principal Component Analysis

4.2.1 Background

When spectral data is collected for a sample from an analytical instrument, it will often require hundreds or thousands of data points in order to generate a spectrum. The high magnitude of data collected can often make it difficult to see variances and correlations across multiple samples. Statistical analyses of the large spectral data sets can help to reduce the number of variables present within each sample, as well as provide a means of emphasizing the similarities or differences across samples. Principal component analysis (PCA) is a method often used when the variables (i.e. samples) contain a large number of measurements (i.e. wavenumbers) and are previously known to have a high chance of correlation. Variables within a data set will often contain information that is consistent across other variables resulting in redundant information overshadowing data that is relevant. PCA provides a way to reduce the similarities within the data set while maximizing the variations.[40, 41]

A large data set can be reduced down into what are known as the principal components (PCs). The first principal component (PC1) accounts for the largest amount of variation within the data set, with each additional principal component representing progressively smaller percentages of variation.[39, 40] The eigenvalues, associated with a PC, represent the breakdown of the total variance shared among the principal components, which is calculated from a covariance matrix. Furthermore, the proportion of variance represents the percentage that

each eigenvalue represents within the total variance. The eigenvalues can be used to generate a scree plot, which gives a visualization of which PCs should be used. The number of PCs used for visualization can then be selected based on the percentage of variance represented among them. Typically, the first two or three PCs will encompass a large portion of the variance (~90%). Using the eigenvalues and the coefficients of the principal components, values known as 'scores' can be calculated for each principal component.[40] The values in the resultant data set, i.e. the scores, are therefore not correlated with each other as the variables were within the original data set and can be used to create either a two- or three- dimensional plot of the data groupings.[40, 41]

4.2.2 Data Analysis

Once the raw spectral data was normalized, the four categories, i.e. the full cartridge anvils, the full cartridge cups, the primed only anvils, and the primed only cups, were separated into their own workbook to create four distinct data sets. PCA was performed on each data set using the R Project software and a set of scores was generated for each one. PC1 was plotted against PC2 to generate a two-dimensional plot of the data. The data points were then separated based on two criteria: one plot separated the data by the priming mixture composition, i.e. lead-free or lead-based (Figure 15A), while a second plot showed the separation of data by manufacturer (Figure 15B). If the first two PCs did not represent a high enough proportion of the variance to provide a sufficient separation of the data points, PC3 was included and the data was replotted in three dimensions with PC3 on the Z-axis. As with the two-dimensional plots, the first plots showed the separation of the data by the priming mixture

composition (Figure 16A) while the second plot showed the separation of the data by manufacturer (Figure 16B).

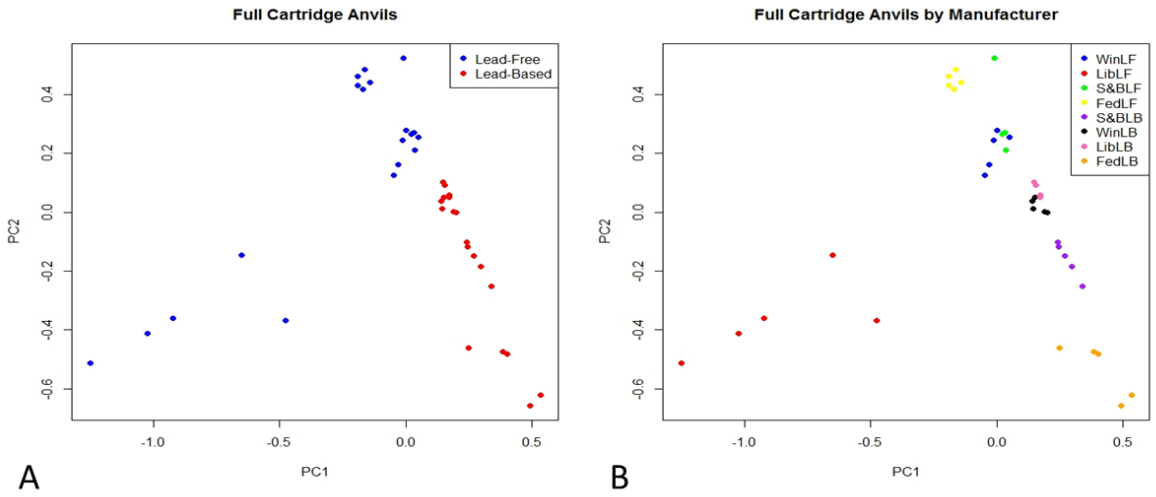


Figure 15: A) PC scores plot showing the data for the full cartridge cups separated by their priming mixture, i.e. lead-free or lead-based. B) PC scores plot showing the data for the full cartridge cups separated by manufacturer.

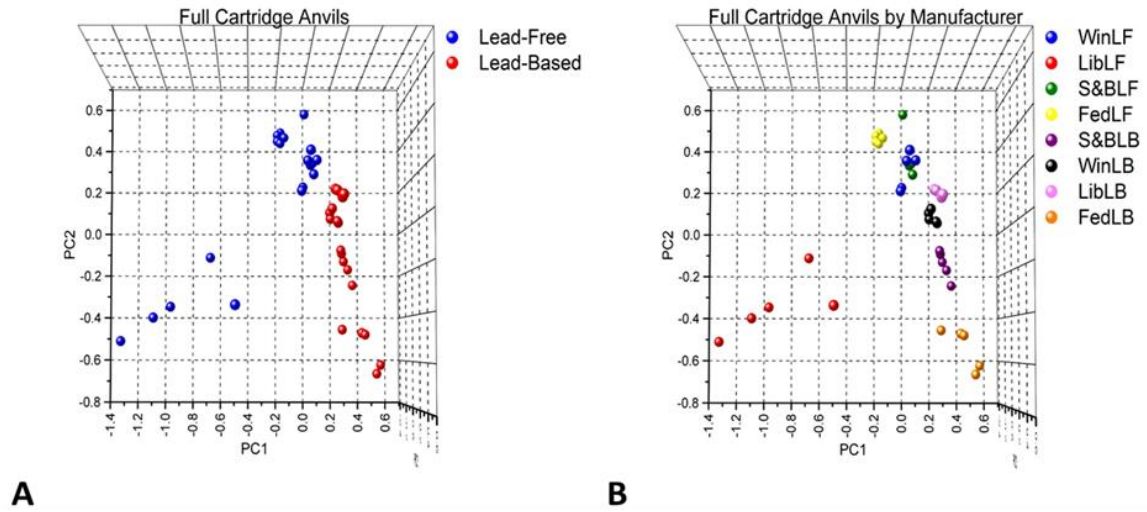


Figure 16: A) PC scores plot showing the data for the full cartridge anvils separated based on their priming mixture, i.e. lead-free or lead-based. B) PC scores plot showing the separation of data based on manufacturer.

4.3 Linear Discriminant Analysis

PCA is a method of determining whether samples fall into groups based on similarities of variables, especially if no prior knowledge is known about the groups to be expected. This is useful for determining what variables may cause of a set of samples to cluster, or separate, into unique groups, e.g. the presence or absence of K may cause data to separate into two groups. Another method of classifying samples is by linear discriminant analysis (LDA). A set of samples with known classifications can be used as 'training objects' for which other samples (i.e. test samples) can be classified against. The 'training objects' can be used to create a model that will provide the framework for classifying unknown samples into a classification. The data for the samples of known classification are combined from a matrix with *n* dimensions into a matrix with one dimension, resulting in a single value for each set of data known as *Y.* The samples of unknown classification, i.e the 'test set', can then be classified according to their *Y* values. A common method of summarizing the results of LDA is a confusion matrix, which shows the known classification of the samples versus the model classification.[40]

4.3.1 Data Analysis

Once PCA was performed on the raw normalized data (refer to Section 4.2 Principal Component Analysis), the scores were used to create the LDA model for classifying training samples. As the anvils showed better separation based on the PCA, only the anvils were used for the LDA methodology. LDA was performed on the full cartridge dataset, the primed only dataset, and a combined matrix of the two datasets. The samples were separated into two groups, LFP or LBP, and LDA was performed using *k*-fold cross-validation with five folds and ten

repeats. The samples were separated into five sets with each set containing eight samples (i.e. 20% of the data). The first set (or *fold)* was withheld and the remaining samples were used to create a model set (i.e. training set). The classifications of the withheld samples were then predicted by the training set. The first set was then returned to the training set and the procedure was repeated with the second set withheld, and so on until each of the five sets were withheld once.[42] This whole procedure was then repeated ten times which resulted in 400 variables instead of the original 40. The results were summarized in confusion matrices that showed the results for the full and primed only anvils, as well as another confusion matrix which shows the results for the combined matrix of the full and primed only datasets. In addition, a secondary dataset of samples not previously used was tested against each model to determine the classification capability of the models. These results were summarized in a second set of confusion matrices, one for each of the models.

CHAPTER 5: RESULTS AND DISCUSSION

LFPs are becoming more popular as the health concerns associated with the inhalation of lead become more prevalent. The use of LFPs in ammunition, as opposed to their lead-based counterparts, results in residue both physically and chemically different from TGSR. Ammunition containing LFPs is, therefore, not easily identifiable by traditional methods, i.e. the criteria outlined by ASTM International. While research has been conducted on the differences between LFP and LBP muzzle discharge residue, there is little research on the origin of the defining characteristics between them. This research aims to outline the characteristics associated with both types of ammunition by analyzing the residue that is left behind in the priming cup. The priming cup residue will aid in determining what occurs during the ignition process and what components of the primer and cartridge case may contribute to the muzzle discharge residue.

Both a lead-based and lead-free ammunition was purchased from four different manufacturers, resulting in eight different ammunitions used for testing (see Table 1). Half of each ammunition had the bullet and smokeless powder removed, and the full and primed only cartridges were fired down range. The fired cartridges were then collected and the priming cup assembly was removed from the base of the cartridges. Five cups and their anvils were adhered to aluminum stubs using colloidal graphite and analyzed via SEM-EDX.

5.1 Residue Images

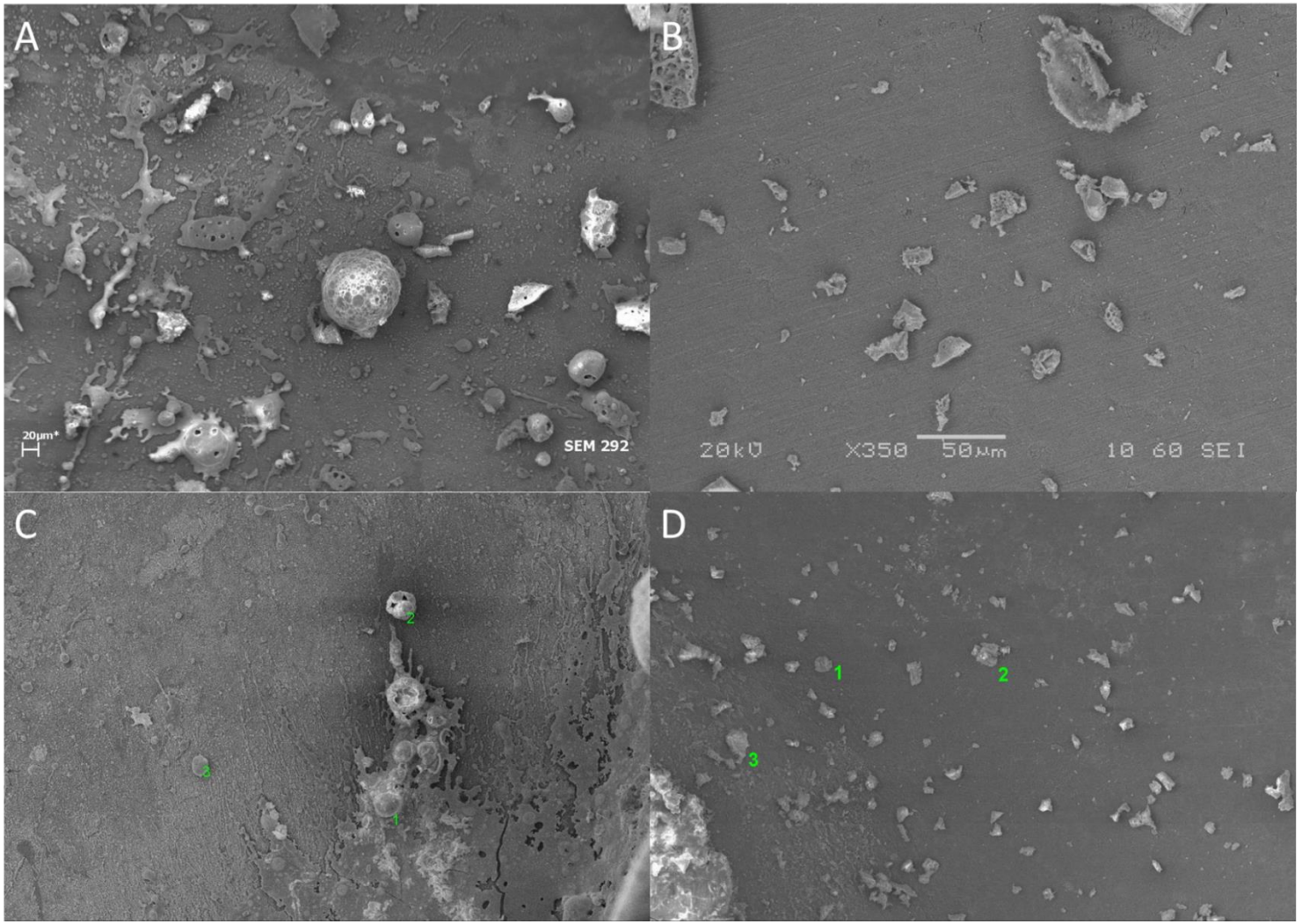


Figure 17: Lead-Based residue on the base of the priming cups. The numbers indicate the particles from which spectra were collected. A) Federal B) Sellier & Bellot C) Winchester D) Liberty

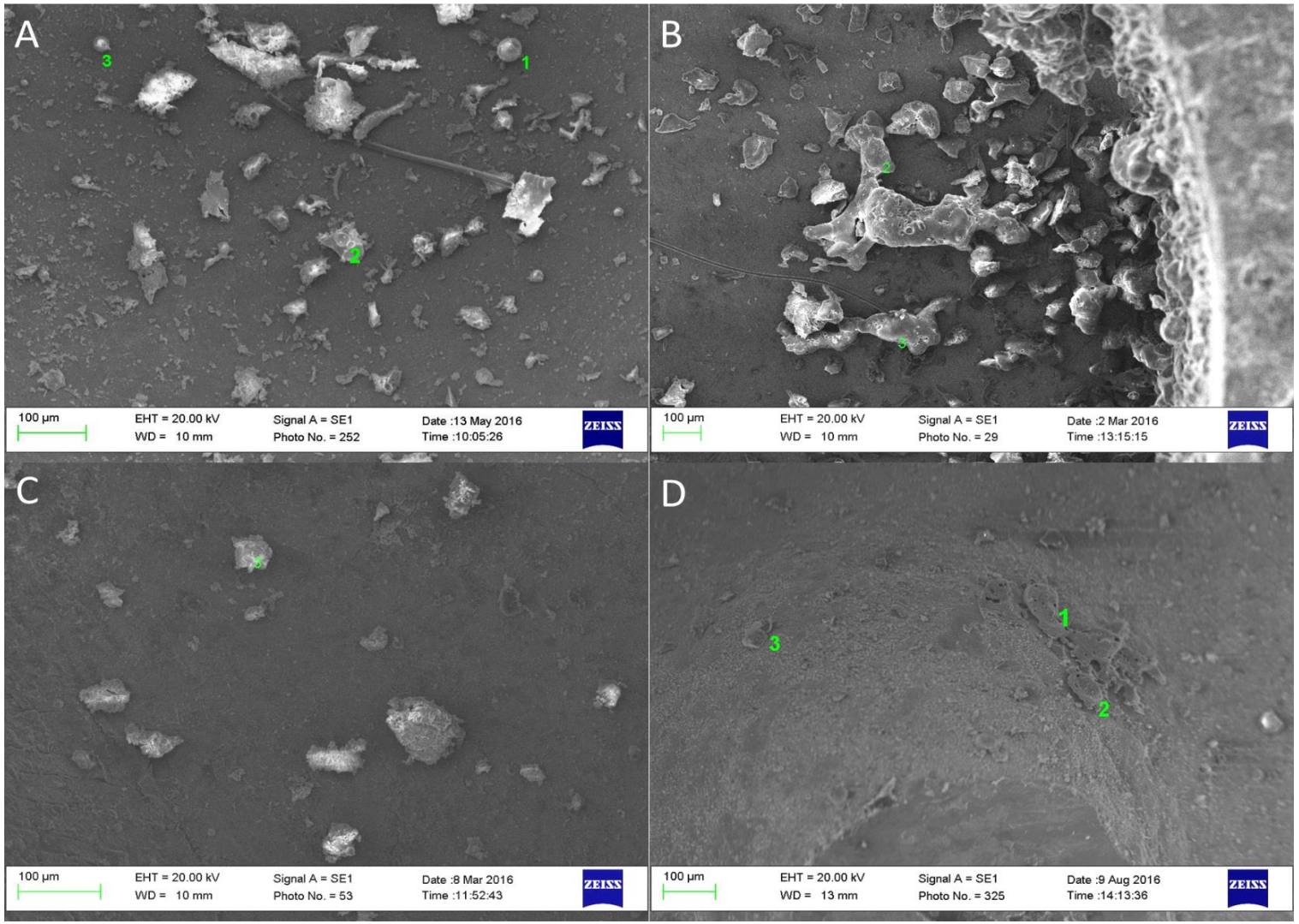


Figure 18: Lead-Free Residue on the base of the priming cups. The numbers indicate the particles from which spectra were collected. A) Federal B) Sellier & Bellot C) Winchester D) Liberty

The post-fire residue left in the base of the priming cups from each type of ammunition is shown in Figure 17 and Figure 18. Figure 17 shows the residue left from those ammunitions which contain LBP, while Figure 18 shows the residue from LFP. Figure 17A shows a large spherical globule with pockmarks; pockmarks indicate that gases were formed during detonation and gas bubbles formed within the particle. Figure 17A and Figure 17C both show structures that appear as if a foam was created from the detonation of the primer, while Figure 17B and Figure 17D both appear to have fairly clean bases covered with loose particles. While all four images are from lead-based ammunitions, the resulting residue has no real definitive characteristics.

Similarly, Figure 18 shows no real consistency across the different residues, but does show that the resulting residue is irregular in shape, as opposed to the LBP which do contain the occasional spherical particle. Typically with LBP ammunition the particles are spherical in shape (refer to Section 2.3 Gunshot Residue Identification), however the residue may not have the space to form spherical particles due to the confined nature of the priming cup as well as the presence of the anvil. When the primer detonates, the residue will either be blocked by the anvil or travel through the flash hole and exit the muzzle of the weapon. The residue that remains will vaporize and condense quickly due to the sudden drop in temperature and pressure after detonation. This results in the residue condensing as films, foaming structures or irregularly shaped particles, rather than the typical spherical particles found in muzzle discharge.

5.2 Lead-Based Ammunition Spectra

The following results show the EDX spectra for the four different types of lead-based ammunition for this research project. The C and O peaks located on the far left of each spectra are a results of atmospheric conditions, as well as the organic components of GSR which are unidentifiable in an EDX. The priming cups shows considerably less residue due to the high walls blocking the x-rays from reaching the detector. The anvils hold the majority of the residue as they are in the direct path of the residue when it is detonated.

5.2.1 Federal Lead-Based

Analysis of the Federal lead-based EDX spectra (Figure 19 and Figure 20) shows the presence of those components typically associated with lead-based ammunition. Pb originating from the explosive is present in both the full cartridge and primed only ammunitions, as well as the Sb originating from the fuel. These two components are consistent with the lead styphnate and antimony sulfide listed in the material safety data sheet (MSDS). In addition to these two primary components is the presence of Ba, though it appeared more abundant in the full cartridge as opposed to the primed only. The MSDS also lists the presence of Cu, Zn, and Al. Although the Cu and Zn were abundant in both types of ammunition, the Al was only present in the full cartridge ammunition, though the intensities of the peaks are low compared to the other component. Because brass is a Cu/Zn alloy, the Cu and Zn may also originate from the brass anvils and priming cups which may liquate on detonation of the priming mixture. Small peaks of Ni were also identified in the cups which may originate from the Ni plating on the priming cup, or the Ni located in the priming mixture.

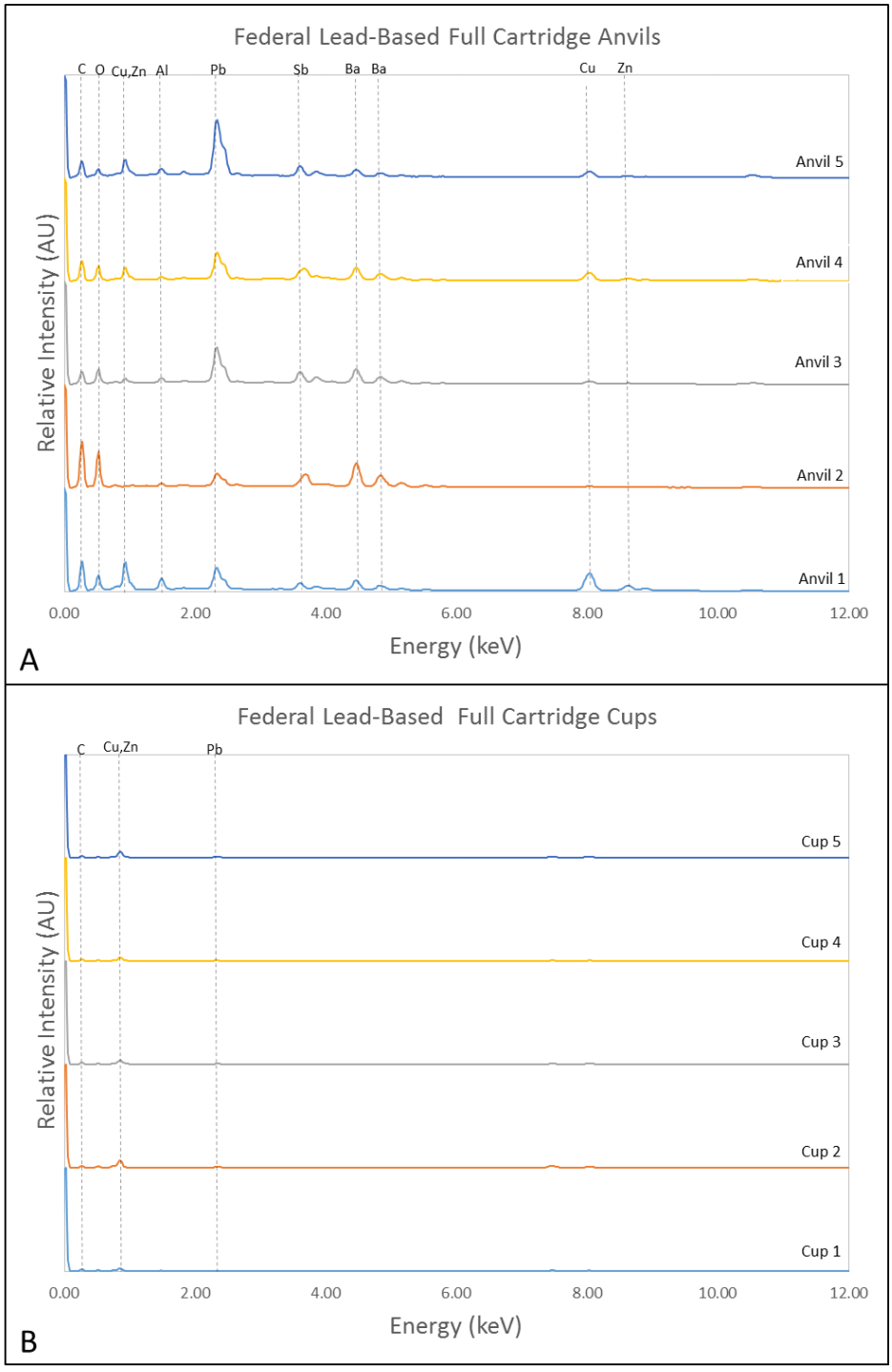


Figure 19: A) EDX spectra for the Federal lead-based full cartridge anvils B) EDX spectra for the Federal lead-based full cartridge cups

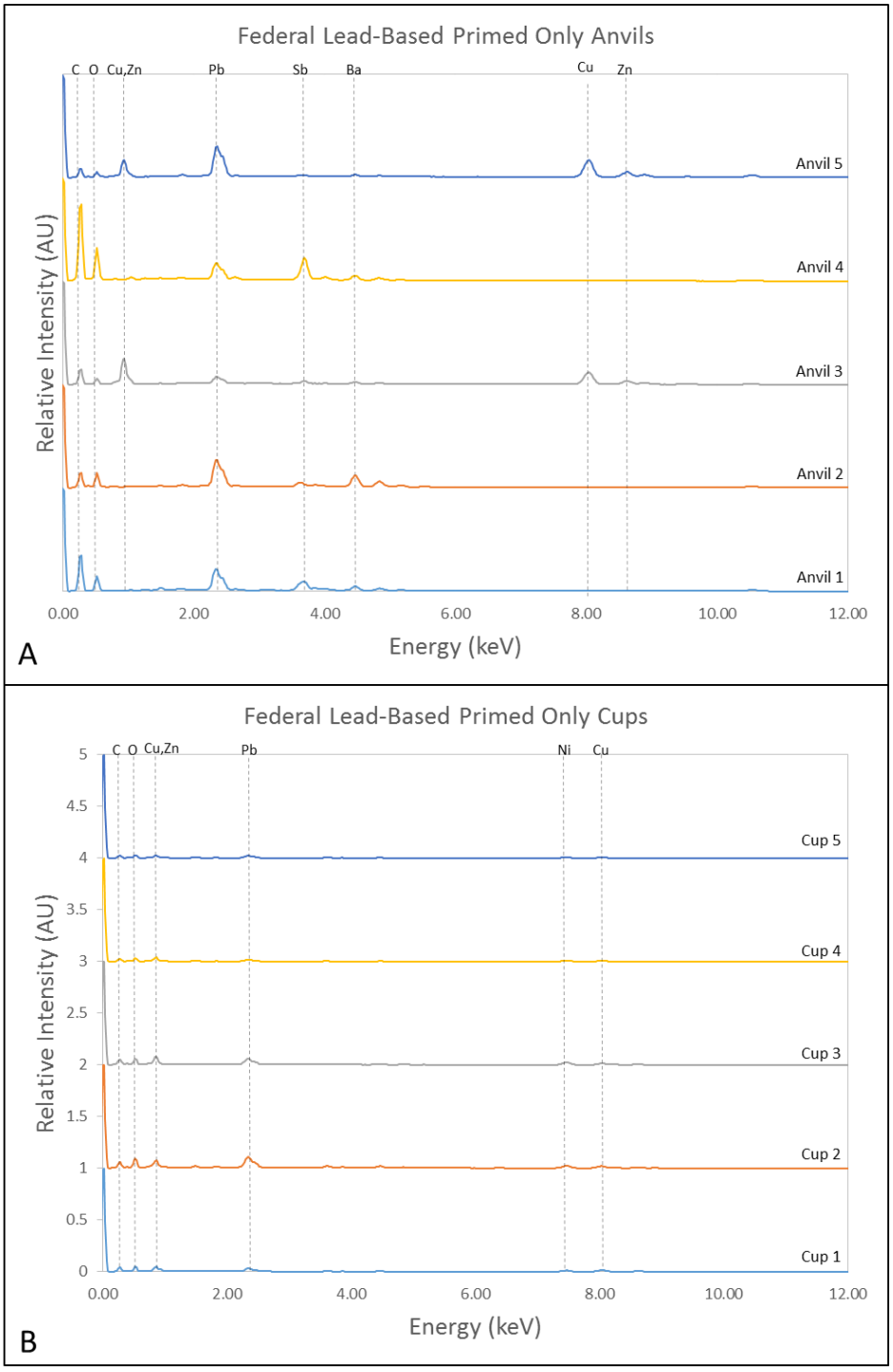


Figure 20: A) EDX spectra for the Federal lead-based primed only anvils B) EDX spectra for the Federal lead-based primed only cups

5.2.2 Liberty Lead Based

The EDX spectra for the Liberty lead-based ammunition (Figure 21 and Figure 22) is different from that of typical lead-based ammunitions, as it does not show the presence of Sb. Neither the full cartridge nor the primed only cartridges indicate the present of Sb, which is consistent with the absence of Sb listed in the MSDS. Pb and Ba, however, are consistent with the lead styphnate and Ba listed in the MSDS. Cu and Zn are also present, which may originate from the priming mixture or the liquation of the brass priming cup and anvil. The spectra do show the presence of both Al and Ca, while not listed in the MSDS these may act as either a fuel or a frictionator in the priming mixture.[3]

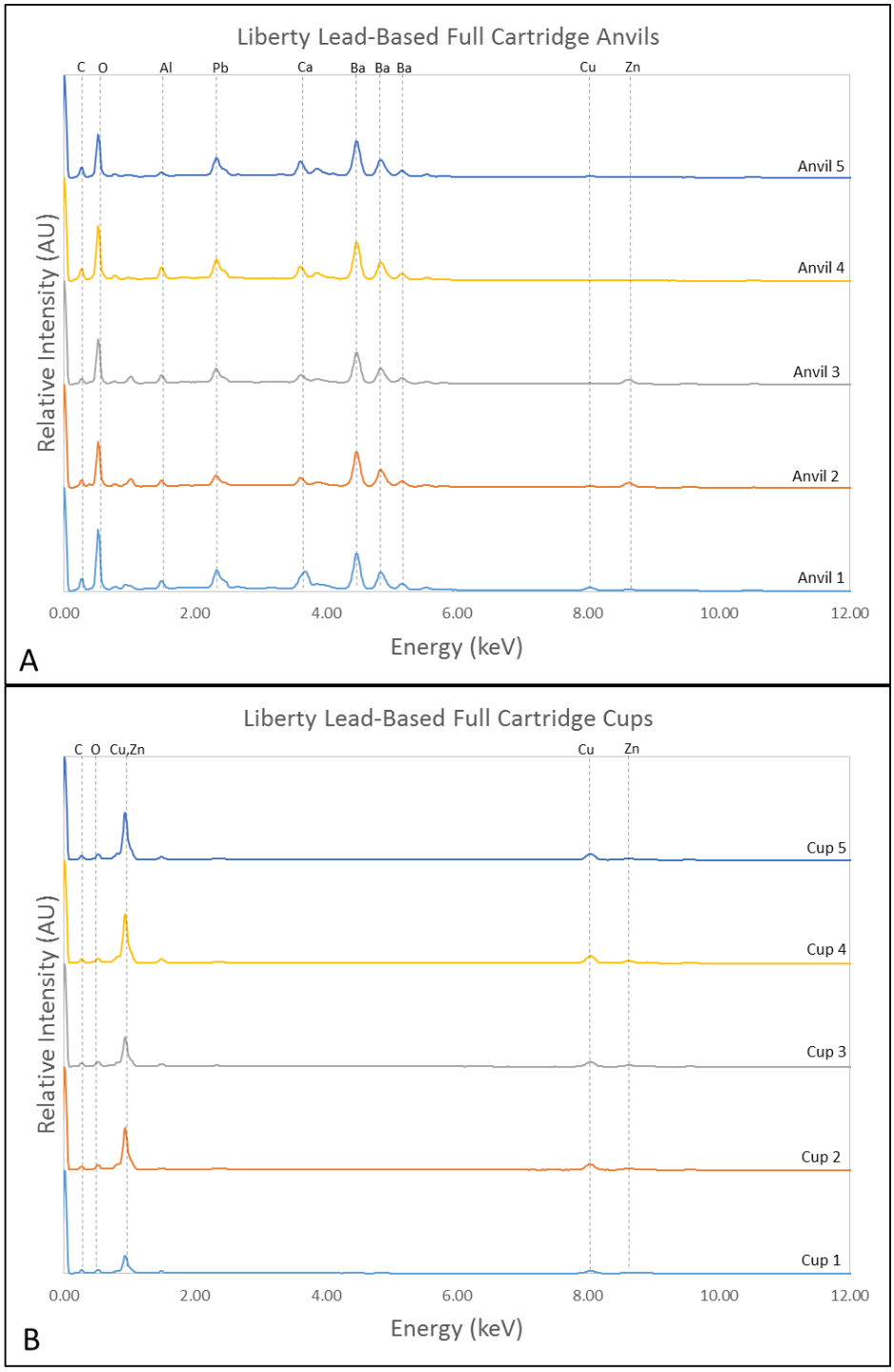


Figure 21: A) EDX spectra Liberty lead-based full cartridge anvils B) EDX spectra for Liberty lead-based full cartridge cups

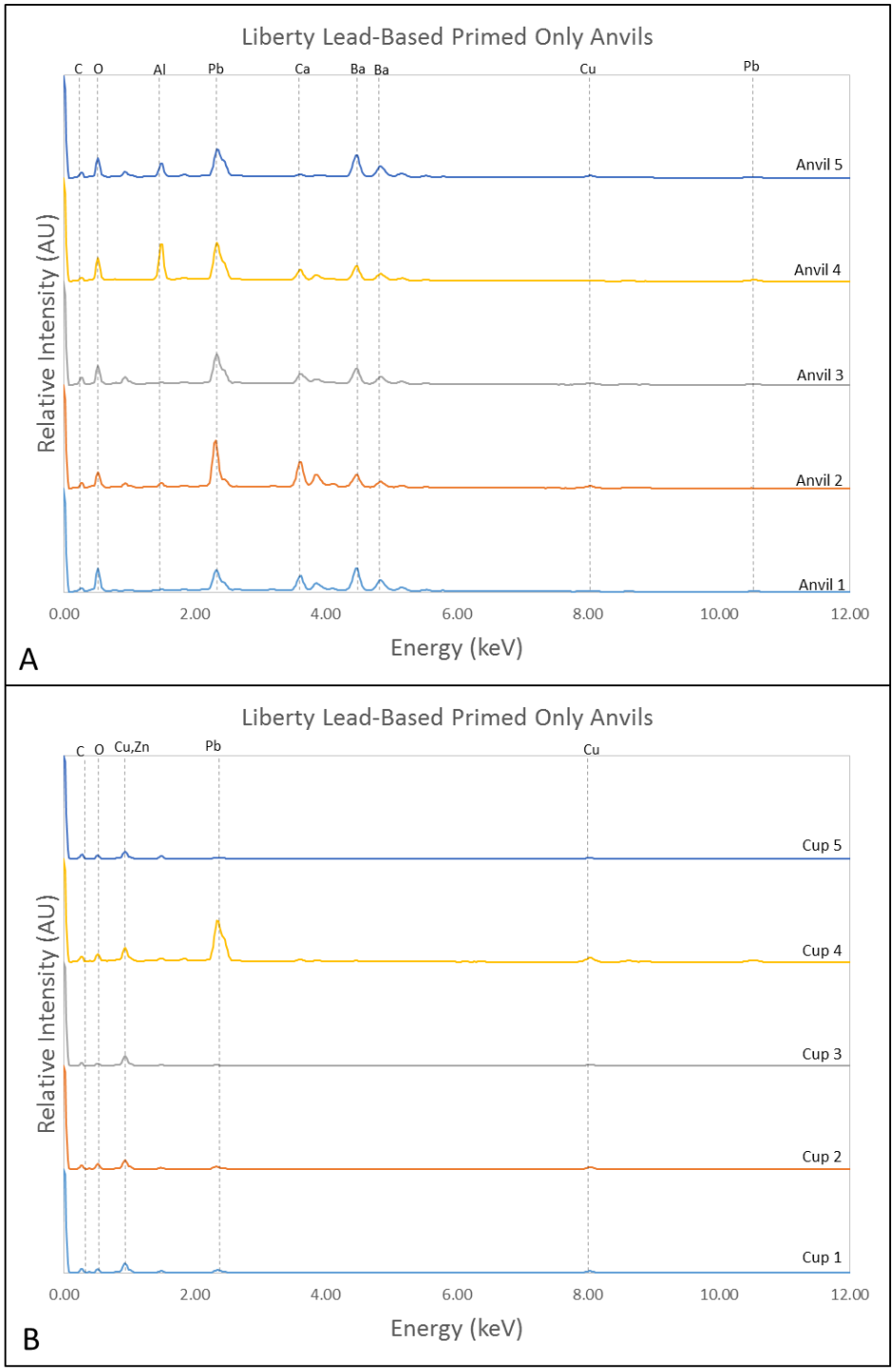


Figure 22: A) EDX spectra for Liberty lead-based primed only anvils B) EDX spectra for Liberty lead-based primed only cups

5.2.3 Winchester Lead-Based

According the MSDS for Winchester ammunition, the primer is a very traditional mixture. The EDX spectra (Figure 23 and Figure 24) indicates the present of Pb, Ba, and Sb, which are consistent with the lead styphnate, antimony sulfide, and barium nitrate in TGSR. The spectra for both the full and primed only cartridges are very similar, with the primary difference being the quantity of barium present. Barium is much less abundant in the primed only ammunition. The MSDS also lists the presence of lead thiocyanate which may contribute the abundance of lead present in the sample. Apart from the three primary elements consistent with GSR, this ammunition also showed the presence of Cu and Zn, primarily in the full cartridges. According to the composition of the ammunition, Cu and Zn are present in the shellcase. This indicates that the Cu and Zn present in the residue is likely to have originated from the brass priming cup, which is not Ni plated in this ammunition, as well as the brass anvil.

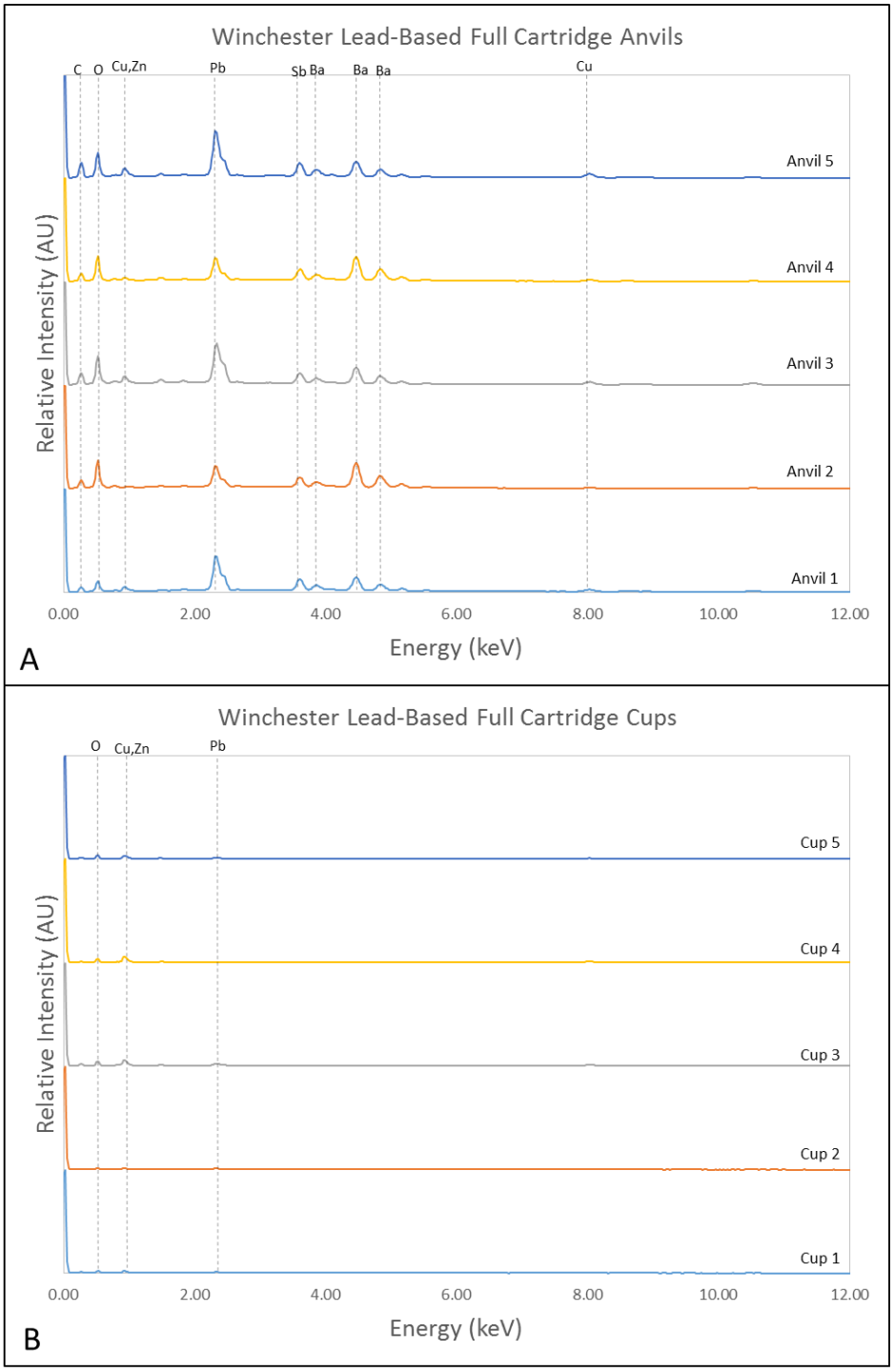


Figure 23: A) EDX spectra for Winchester lead-based full cartridge anvils B) EDX spectra for Winchester lead-based full cartridge cups

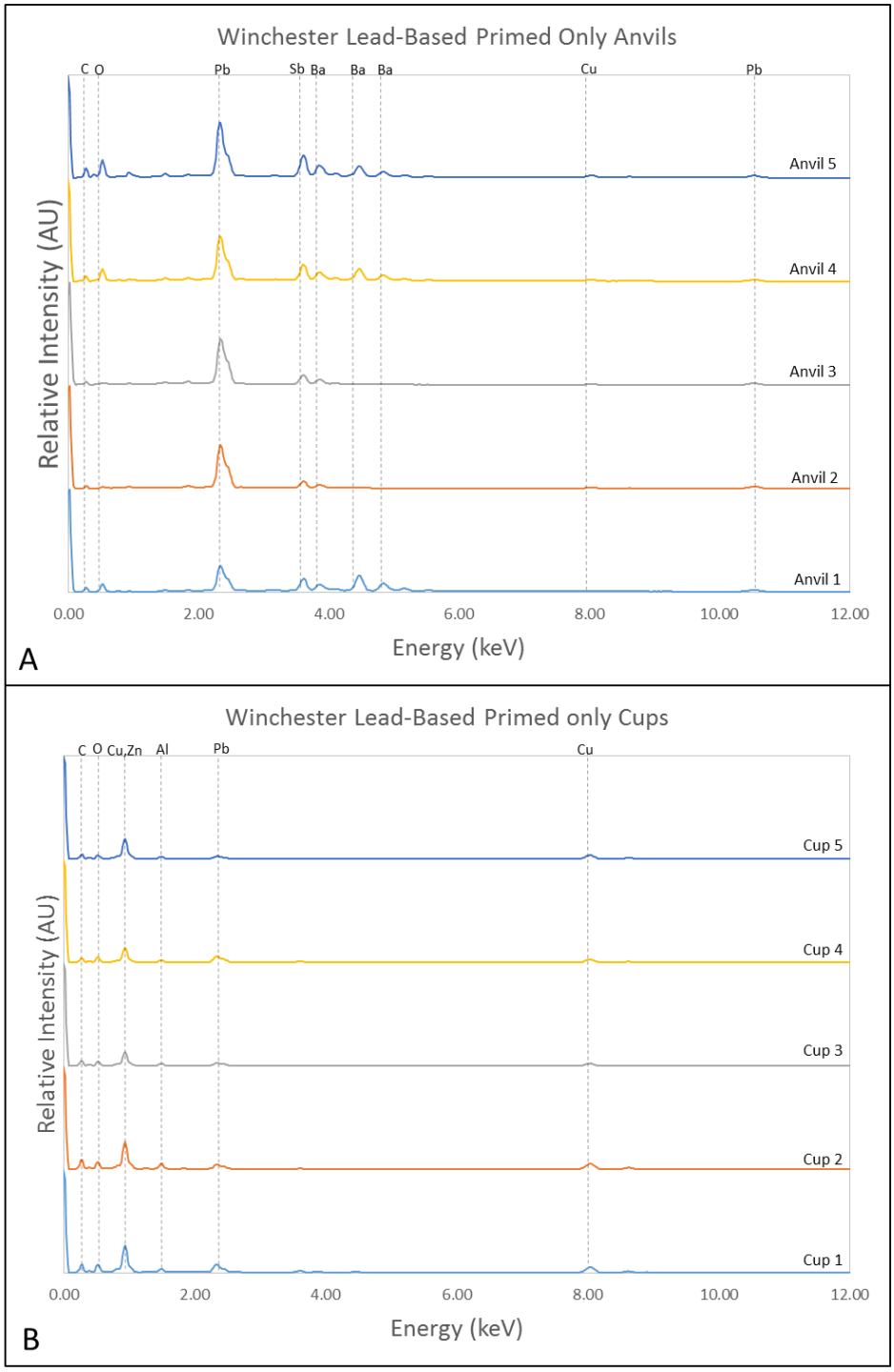


Figure 24: A) EDX spectra for Winchester lead-based primed only anvils B) EDX spectra for Winchester lead-based primed only cups

5.2.4 Sellier & Bellot Lead-Based

Similar to the Winchester lead-based ammunition, the Sellier & Bellot MSDS shows a very traditional priming mixture containing lead styphnate, barium nitrate, and antimony trisulfide. The presence of Pb, Ba, and Sb can be seen in the EDX spectra (Figure 25 and Figure 26) in relatively high abundance. The exceptionally high abundance of lead is due to the addition of several lead oxides to the priming mixture, e.g. lead oxide and lead dioxide. The priming cup is composed of brass, without a Ni plating, as is the anvil. The priming cup and anvil contribute to the presence of Cu and Zn in the residue. This residue also showed the presence of Al, however, this was unlisted in the MSDS indicating it may act as an additive as part of the fuel or a frictionator.[3]

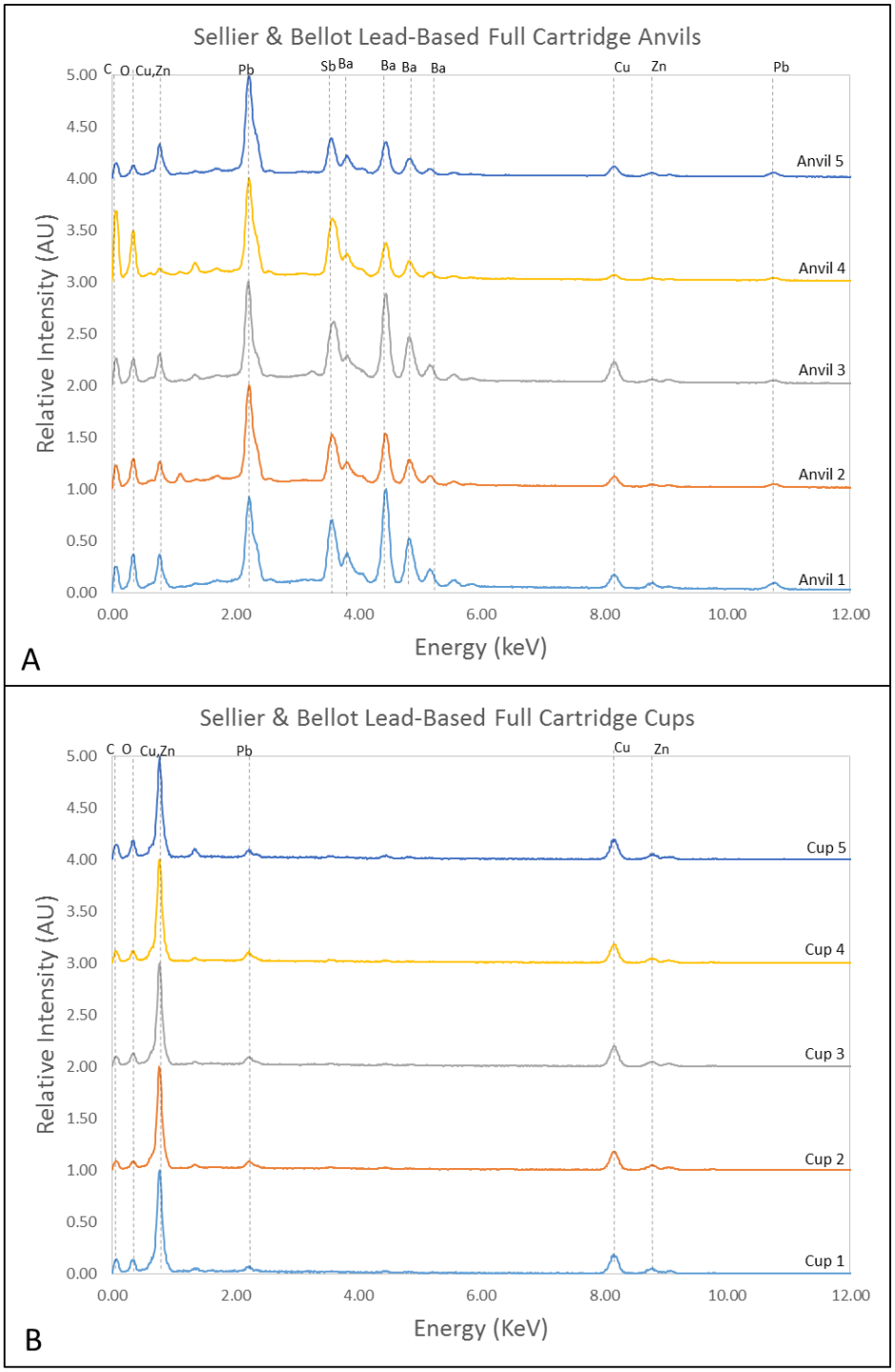


Figure 25: A) EDX spectra for Sellier & Bellot lead-based full cartridge anvils B) EDX spectra for Sellier & Bellot lead-based full cartridge cups

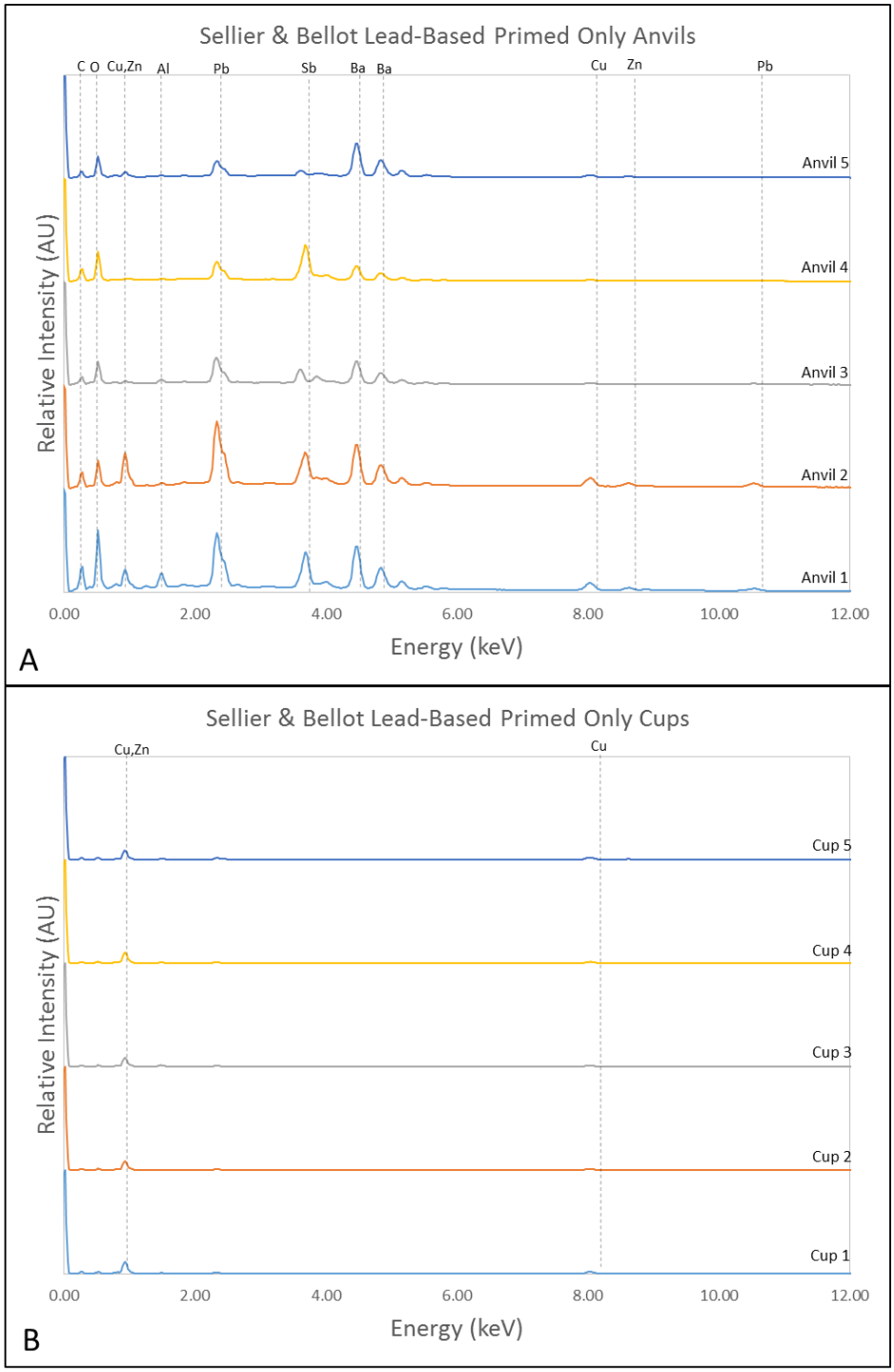


Figure 26: A) EDX spectra for Sellier & Bellot lead-based primed only anvils B) EDX spectra for Sellier & Bellot lead-based primed only cups

5.3 Lead-Free Ammunition Spectra

The following results show the EDX spectra for the four different types of lead-free ammunition for this research project. The C and O peaks located on the far left of each spectra are a results of atmospheric conditions, as well as the organic components of GSR, which are unidentifiable in an EDX. The priming cups shows considerably less residue due to the high walls blocking the x-rays from reaching the detector. The anvils hold the majority of the residue, as they are in the direct path of the residue when it is detonated. The lead-free ammunitions are considerably different from their lead-based counterparts.

5.3.1 Federal Lead-Free

The EDX spectra for the Federal lead-free ammunition (Figure 27 and Figure 28) are slightly inconsistent with the components listed in the MSDS. The MSDS shows the presence of antimony in the priming mixture, whereas the EDX show the presence of Ti in the full cartridges and Ba in the primed only cartridges, neither of which are listed in the MSDS. The Ba and Ti peaks have energies so close together that although the EDX software identified the peaks as Ba, they may in fact be Ti. This would provide more consistency with the lead-free nature of the primer. In addition, the MSDS shows the presence of a zinc oxide, likely in place of the barium nitrate as the oxidizer, however Zn appeared in the spectra in too low of intensities as to be deemed significant. Similarly, Al and Si were detected in nearly all of the samples, but was not listed as an ingredient in the priming mixture. The primary similarity between the spectra and the list of ingredients is the presence of Ni which is likely to have originated from the Ni plating on the priming cups, as it was only detected in the cups and not on the anvils.

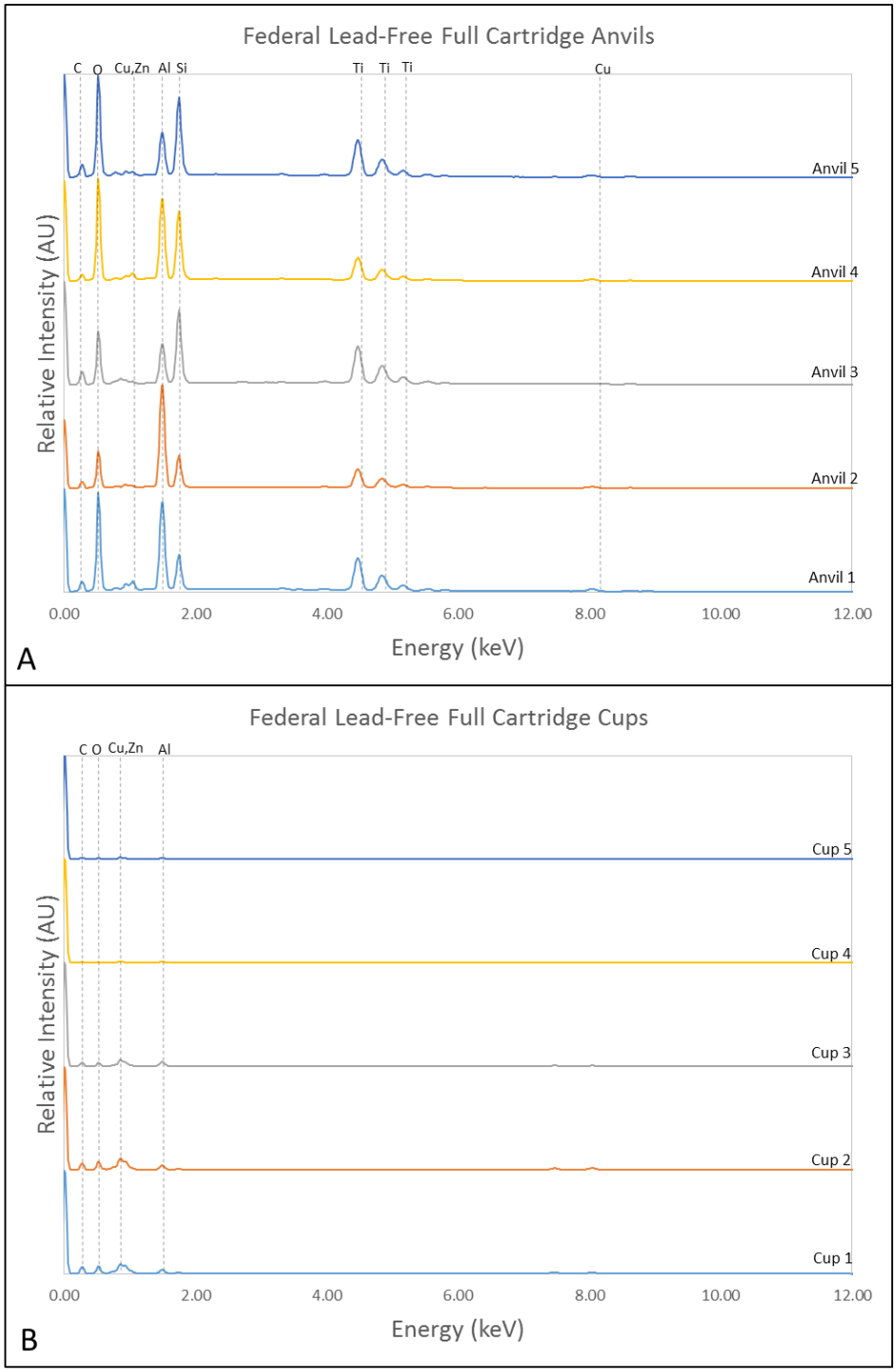


Figure 27: A) EDX spectra for Federal lead-free full cartridge anvils B) EDX spectra for Federal lead-free full cartridge cups

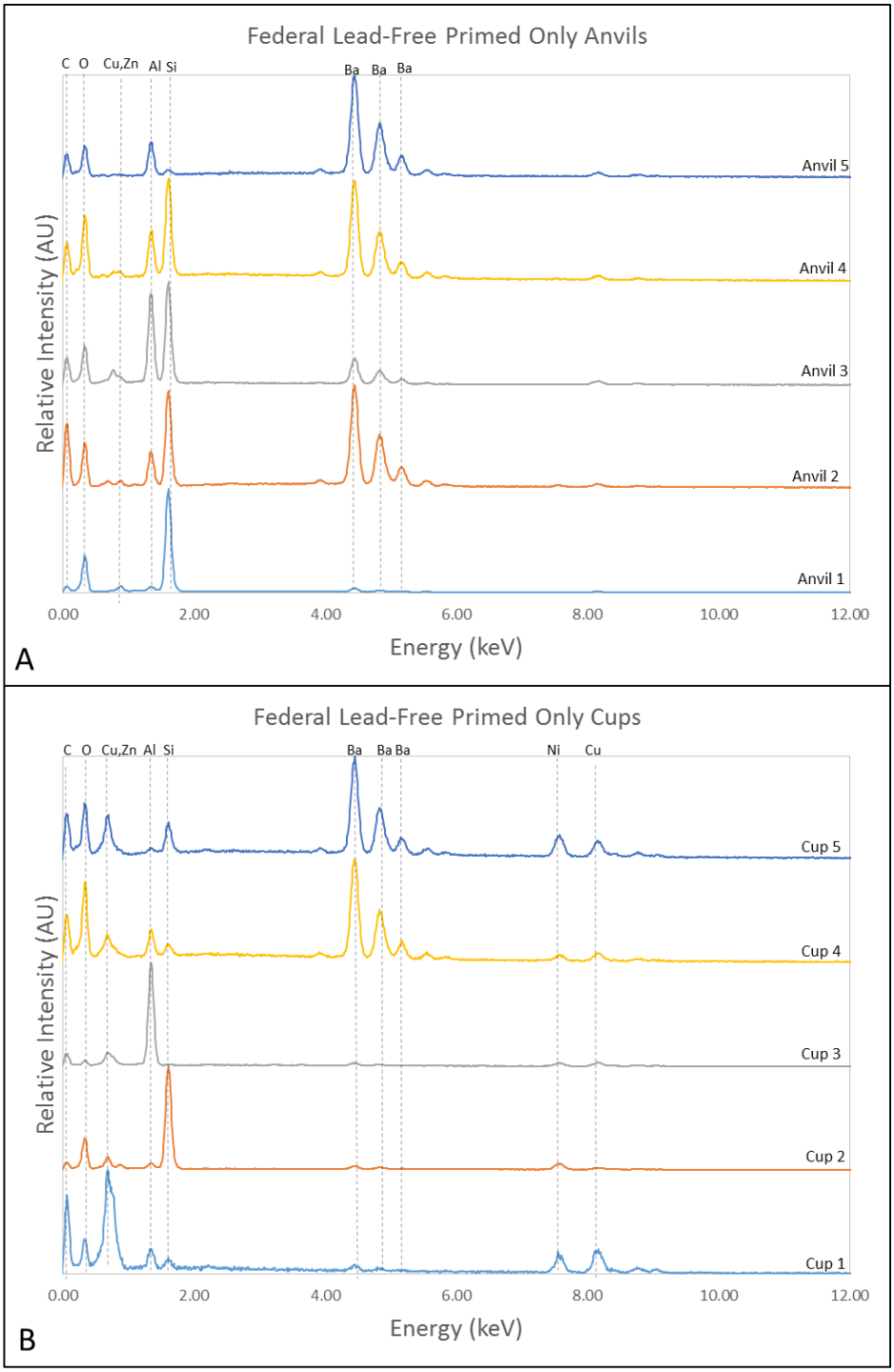


Figure 28: A) EDX spectra for Federal lead-free primed only anvils B) EDX spectra for Federal lead-free primed only cups

5.3.2 Liberty Lead-Free

The MSDS for the lead-free Liberty ammunition provides very little information on the composition of the priming mixture. The single component listed in the mixture is NG which is known to be a part of the smokeless powder rather than the primer. By looking at the EDX spectra (Figure 29 and Figure 30) the composition of the primer can be inferred. The residue contains Cu and Zn which likely originate from the brass cup and anvil, as well as, small peaks for Ni which originate from the Ni, plating on the priming cup. The residue also contains titanium, which is likely used as an alternative for fuel, and Ca, which may originate from either a fuel or frictionator.

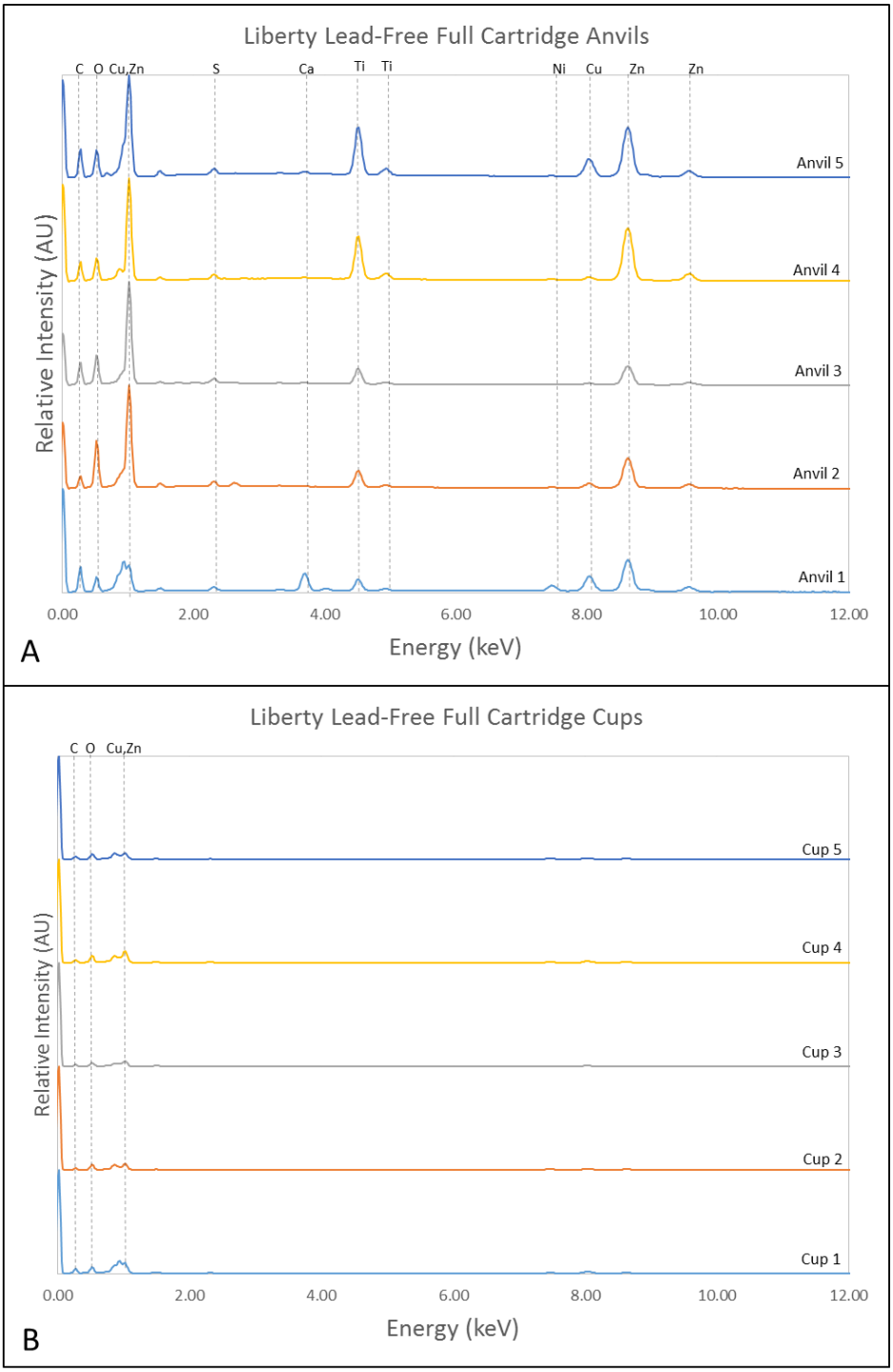


Figure 29: A) EDX spectra for Liberty lead-free full cartridge anvils b) EDX spectra for Liberty lead-free full cartridge cups

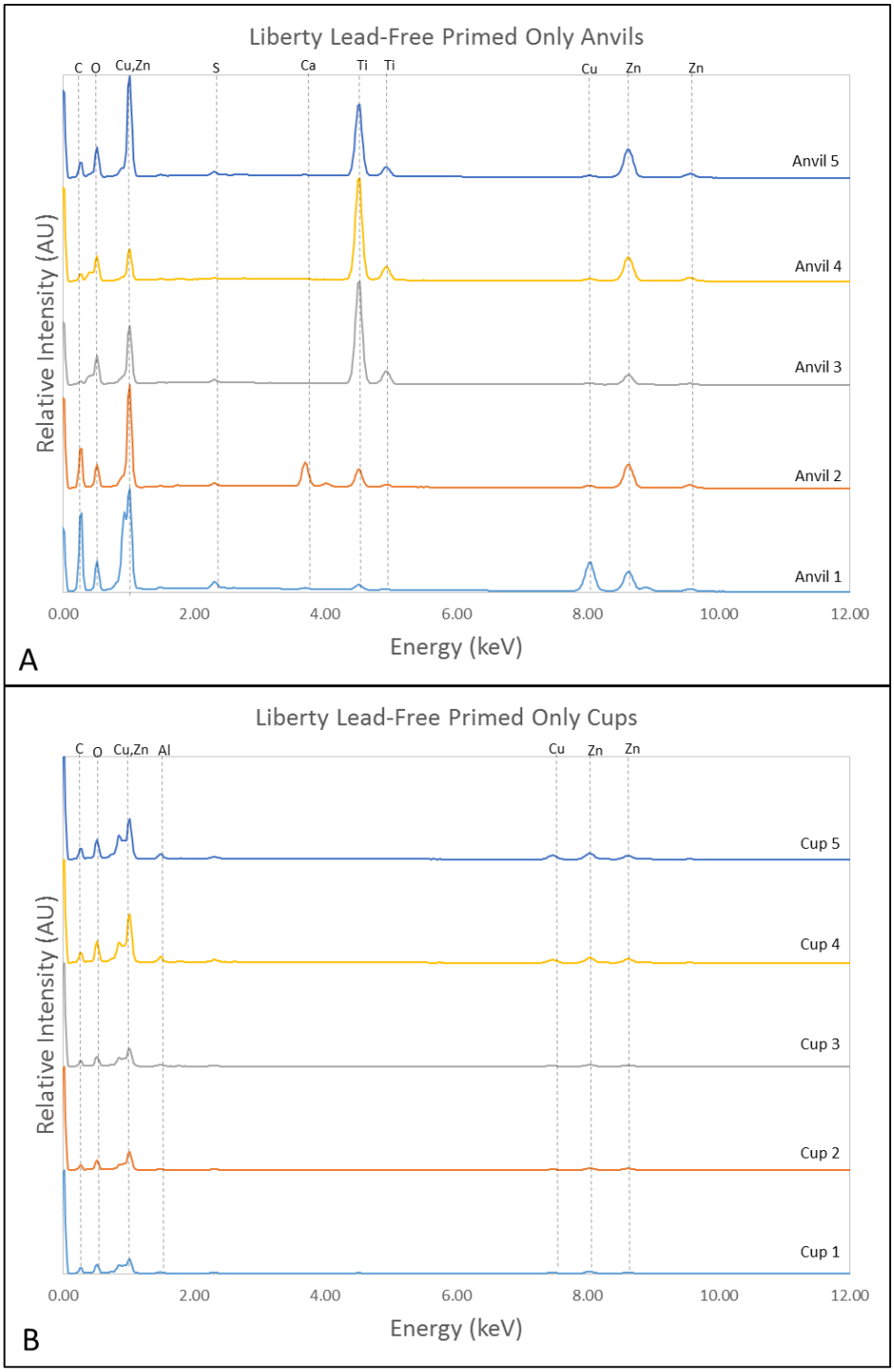


Figure 30: A) EDX spectra for Liberty lead-free primed only anvils B) EDX spectra for Liberty lead-free primed only cups

5.3.3 Winchester Lead-Free

The Winchester lead-free EDX spectra (Figure 31 and Figure 32) show characteristics consistent with the composition of the residue ingredients outlined in the MSDS. K shows a relatively high abundance in both the full and primed only cartridges for the anvils and originates from the potassium nitrate, which acts as an oxidizer in the priming mixture.[3] The mixture also contains DDNP as a replacement for the lead styphnate as the fuel (see Section 2.2 Gunshot Residue Formation), which indicates why the presence of Pb or another Pb replacement is absent from the spectra. DDNP is an organic component, indistinguishable via EDX, as it only contains C and O, which also originate from the atmosphere and the carbon coating. The MSDS also shows the presence of Cu and Zn in the priming mixture, which can be seen in the spectra for both the full and primed only cartridges. The Cu and Zn may also originate from brass anvil and priming cup, though the priming cup for this ammunition is Ni plated as well.

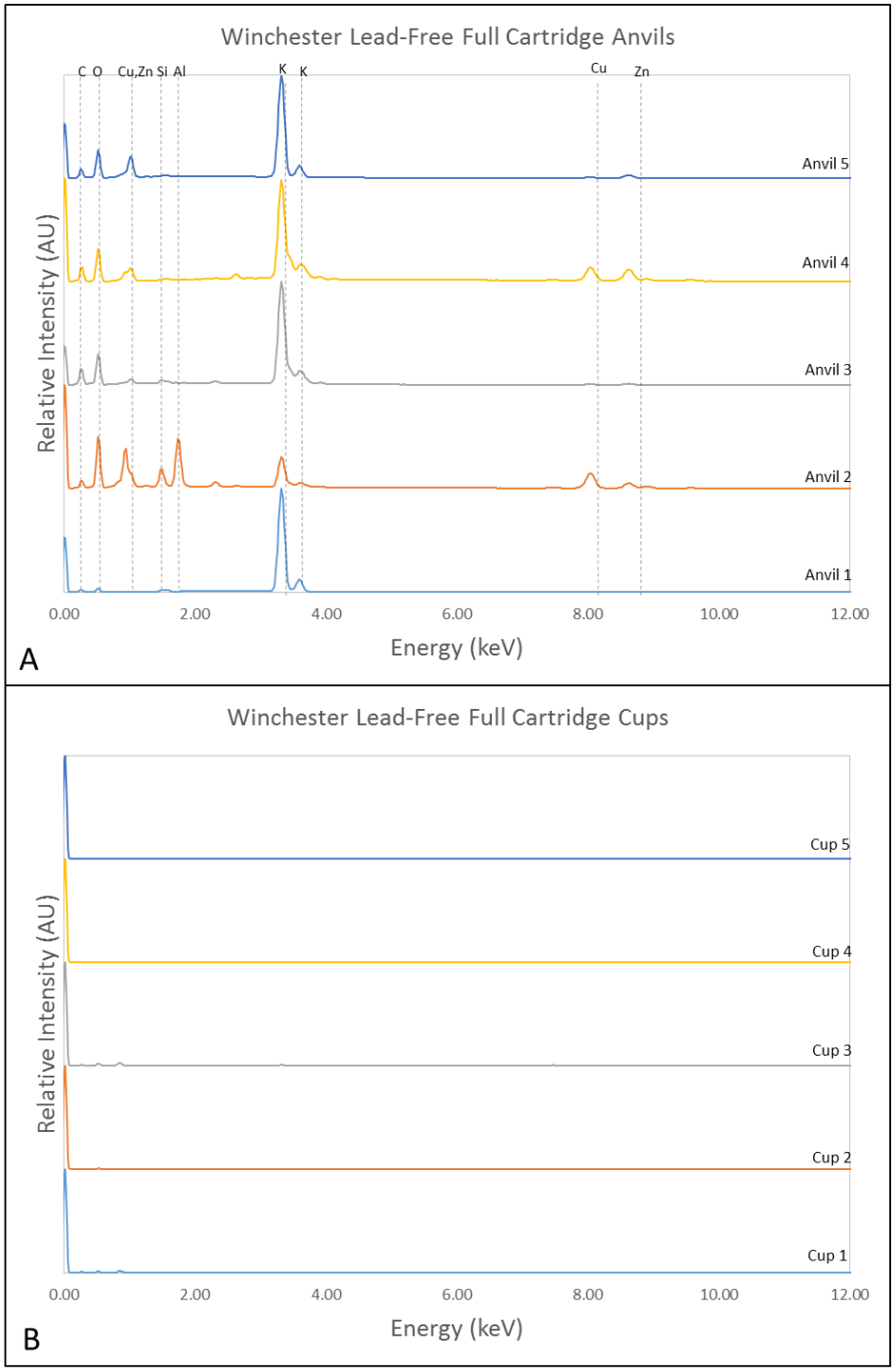


Figure 31: A) EDX spectra Winchester lead-free full cartridge anvils B) EDX spectra for Winchester lead-free full cartridge cups

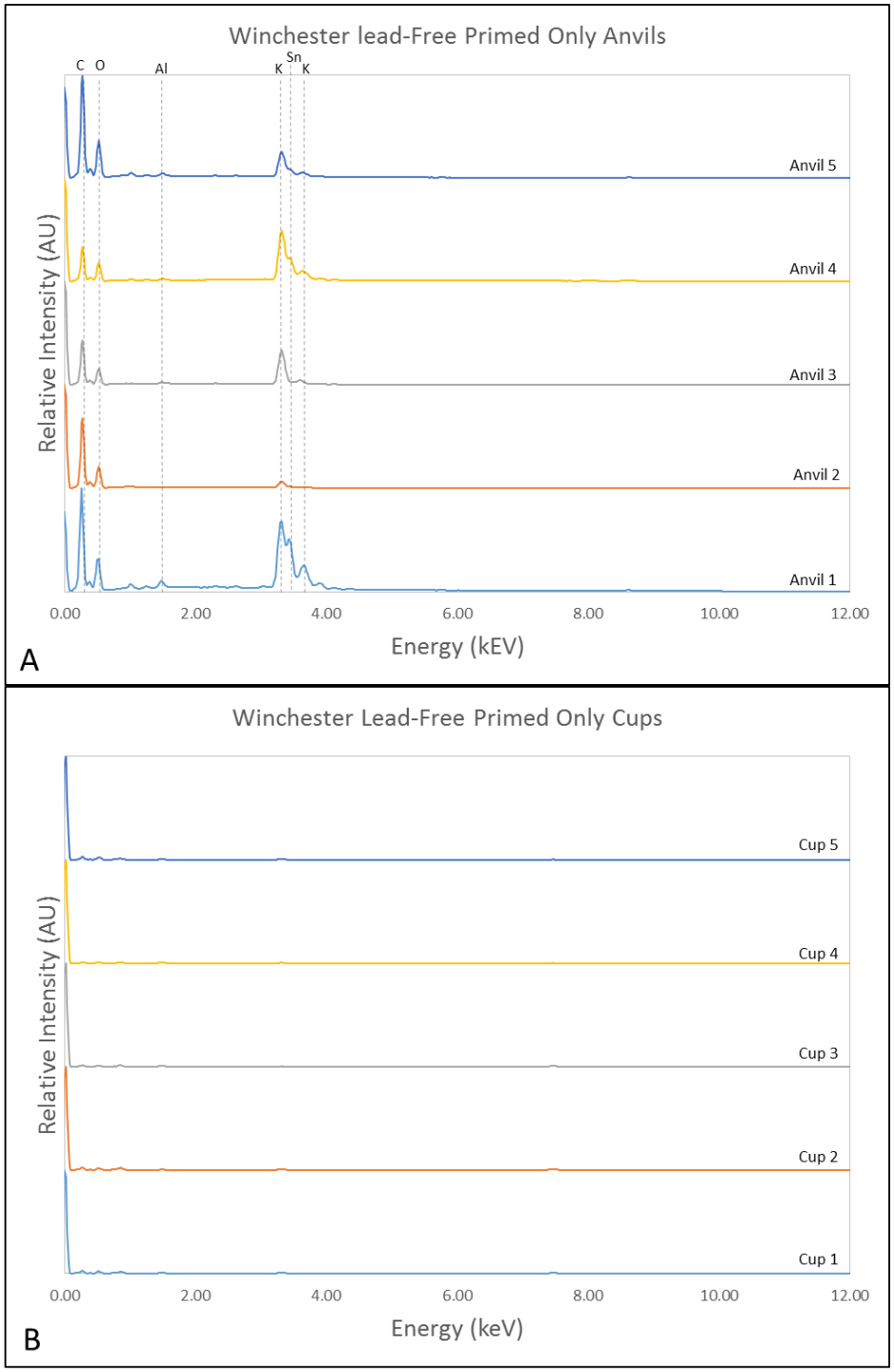


Figure 32: A) EDX spectra for Winchester lead-free primed only anvils B) EDX spectra for Winchester lead-free primed only cups

5.3.4 Sellier & Bellot Lead-Free

The EDX spectra for the Sellier & Bellot lead-free ammunition (Figure 33 and Figure 34) show some similarities the other lead-free ammunitions, such as the presence of K and Si, and the absence of Pb, Ba, and Sb. K, which is present in both the full and primed only cartridges is due to the presence of potassium nitrate, which replaces the barium nitrate as the oxidizer, such as in the lead-free Winchester ammunition. The other primary peak present in the spectra is Si. Although not listed as an ingredient in the MSDS, based on the presence of calcium in the primed only cartridge, this may be present as a calcium silicide to act as a frictionator. This residue also shows the presence of Cu, Zn, and Ni which originate from the brass priming cup and anvil, and the Ni plating present on the brass anvil.

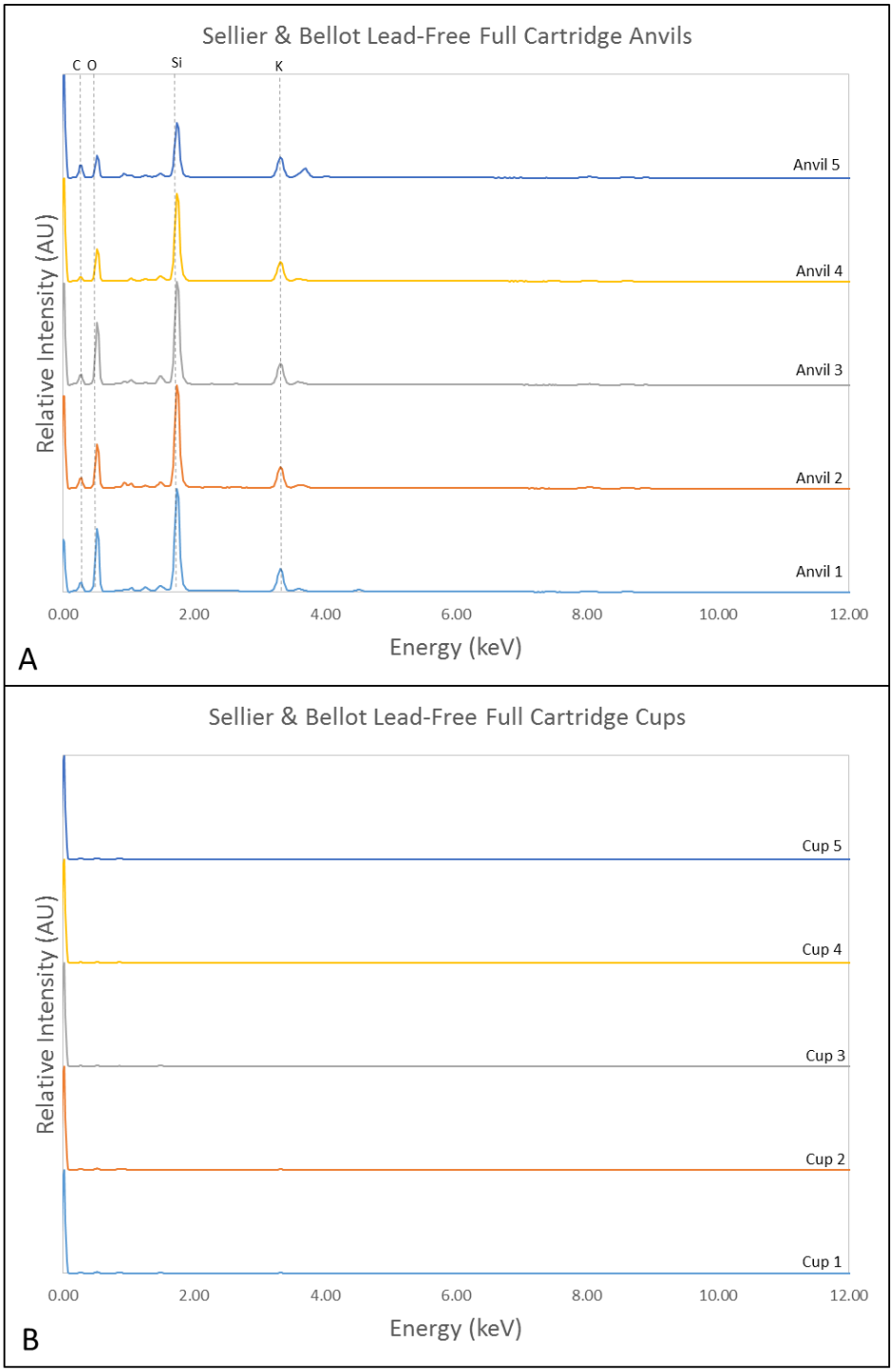


Figure 33: A) EDX spectra for Sellier & Bellot lead-free full cartridge anvils B) EDX spectra for Sellier & Bellot lead-free full cartridge cups

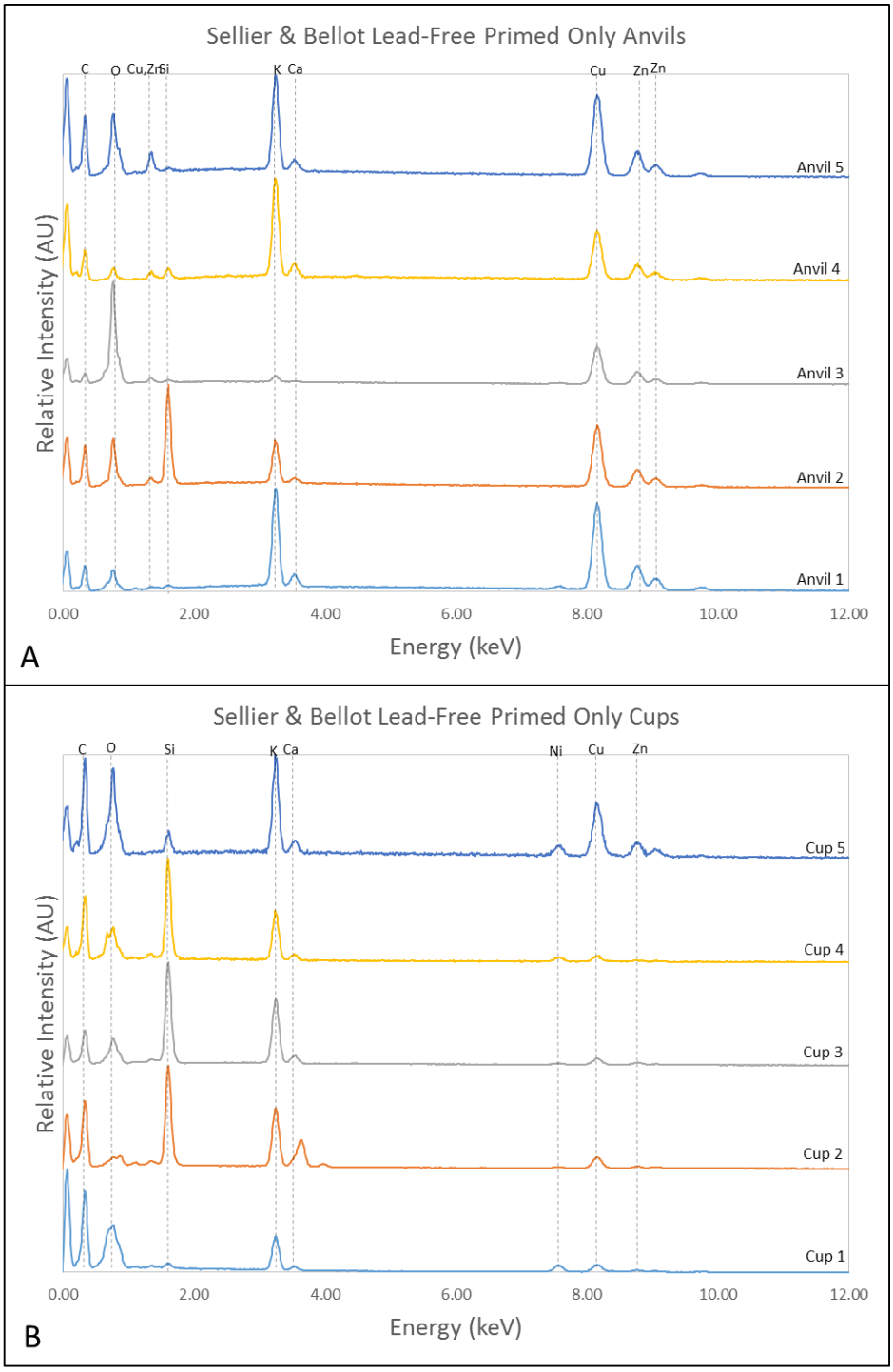


Figure 34: A) EDX spectra for Sellier & Bellot lead-free primed only anvils B) EDX spectra for Sellier & Bellot lead-free primed only cups

5.4 Spectral Comparisons

The LBPs and LFPs showed characteristics consistent with what was expected of each type of ammunition. Three of the four lead-based ammunitions, i.e. Federal, Winchester, and Sellier & Bellot, showed the presence of Pb, Ba, and Sb, which is typically considered indicative of gunshot residue (Figure 19,Figure 20, and Figure 23-Figure 26). The fourth lead-based ammunition, i.e. Liberty (Figure 21 and Figure 22), while similar in composition to the rest, did not have an Sb component to its ammunition, and thus no Sb in its residue. Although a lead-based ammunition, the absence of Sb from the priming mixture sets the Liberty slightly apart from the TGSR standard. In conjunction with this, only one of the four lead-free ammunitions showed the presence of any of these TGSR components, with the Federal lead-free showing peaks for Ba. Pb and Sb were absent from all of the lead-free ammunitions.

A similarity across all both the LBPs and LFPs was the presence of Cu and Zn in varying intensities. While the MSDS for some of the priming mixtures indicates the presence of Cu and Zn in the priming mixture, the priming cups and anvils are also made of brass (a Cu/Zn alloy). The temperature of the priming mixture upon detonation may exceed the melting point of the brass, causing the cup and anvil to liquate and leaving the residue interspersed with Cu and Zn. Another indication of the liquation of the cup is the presence of Ni in many of the spectra, specifically for the cups. Those spectra which showed Ni present (Figure 20, Figure 28-Figure 29, and Figure 34) were consistent with ammunitions that had Ni plated priming cups.

Al is present in both the LBP and LFP spectra (Figure 19-Figure 22, Figure 24, Figure 26-Figure 28, and Figure 31-Figure 32), but is not mentioned in the MSDS for any of the

ammunition as a component of the priming mixture. According to literature, powdered Al can be added to a priming mixture to act as either a fuel or a frictionator.[3] Similarly, Si is present in three of the four LFP ammunitions, i.e. Federal, Winchester, and Sellier & Bellot (Figure 27-Figure 28, Figure 31, and Figure 33-Figure 34), but is not listed as a component in the MSDS. Si can be used in combination with calcium in calcium silicide and be used as either a fuel or frictionator.[3] This can be further shown by the presence of Ca in the Sellier & Bellot residue along with the Si (Figure 32). Additionally, Ti can be used as a replacement for calcium silicide and is present in two of the four lead-free ammunitions, i.e. Sellier & Bellot and Liberty (Figure 27, and Figure 29-Figure 30), but does not appear as a component of the priming mixture in the MSDS.[3] Al, Si, and Ti may all be used as additives in primarily LFP mixture, but are not considered primary components of priming mixture, and thus, aren't listed in the MSDS for the ammunition.

One component of two of the four LFP residues which is consistent with the MSDS is the presence of K (Figure 31-Figure 34). K can be used as potassium nitrate to act as an oxidizer for the replacement of barium nitrate. Barium nitrate is often excluded in those ammunitions which are considered 'toxic metal free', along with the omission of lead, and thus the presence of K is characteristic of a LFP. It is listed as a component in the MSDS for those two ammunitions, the lead-free Winchester and Sellier & Bellot.

5.5 Principal Component Analysis

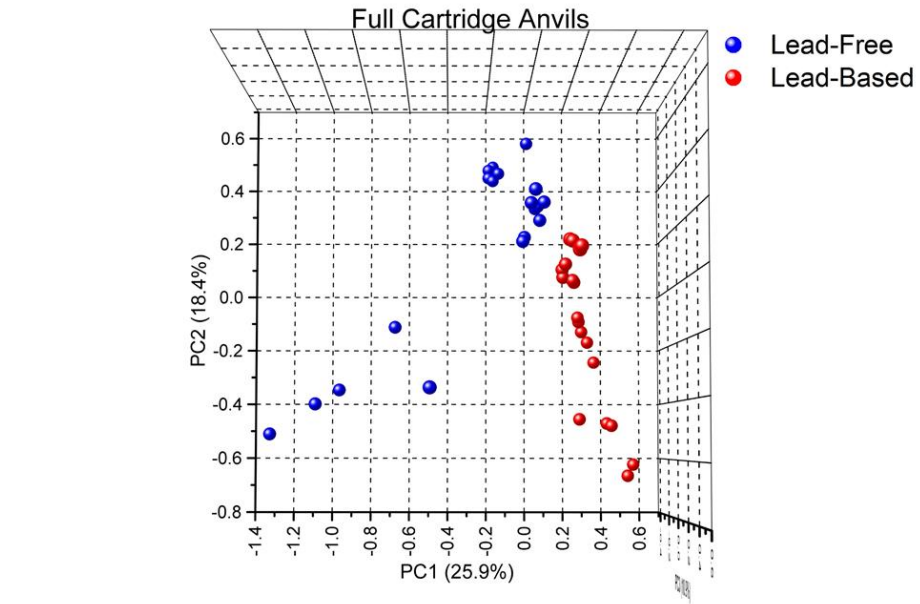
The spectral data was condensed and normalized, and PCA was run on the four different datasets (see CHAPTER 4: STATISTICAL ANALYSIS). Factor loadings and scores were plotted for each dataset. These were used to determine the differences and correlations between ammunitions, both by priming mixture composition and manufacturer. Due to the high walls of the priming cups, more x-rays were able to be collected for the anvils as opposed to the cups, thus better separation and characterization was acquired based on the anvils.

5.5.1 Full Cartridge Anvils

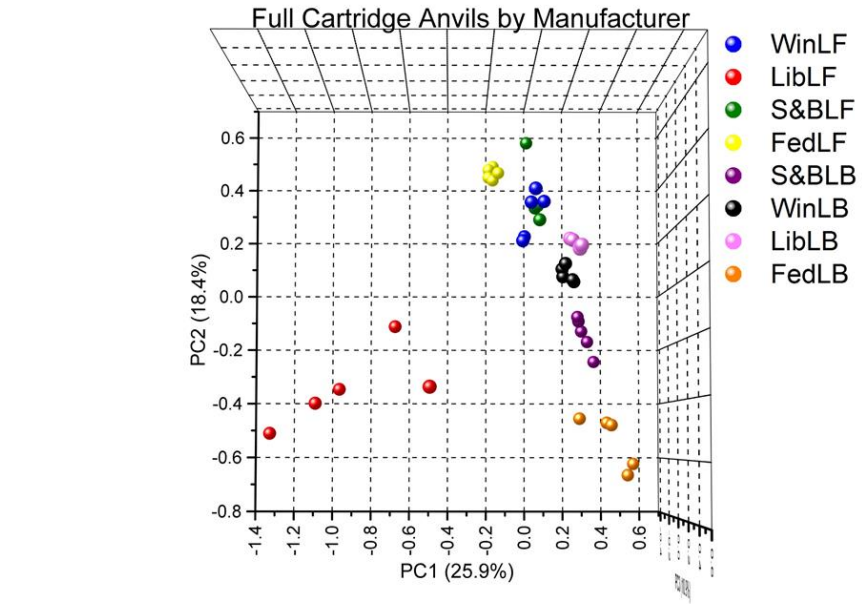
The PCA scores generated for the full cartridge anvils are illustrated in Figure 35 in a three-dimensional plot. Figure 35A illustrates the separation of the full cartridge anvils based upon their priming mixture, i.e. LFP or LBP. Figure 35B illustrates the separation of the full cartridge anvils based upon their primer and manufacturer, i.e. Winchester, Federal, Liberty, and Sellier & Bellot. The factor loadings were then examined to determine the elements that contributed to the variance in the dataset (Figure 36). The loadings plot for PC1 revealed strong positive correlations at energies of 1.823, 2.653, 3.605, 3.844, 3.954, 4.101, 4.466, 4.828, and 5.157 keV, which are indicative of Pb, Ba, and Sb (Figure 36A). Consequently, samples that have large positive scores on PC1 (Figure 35), such as those samples which contain a LBP, contain substantial amounts of Pb, Ba, and Sb. Similarly, the loadings plot for PC1 showed strong negative correlations at energies of 0.832, 2.304, 2.464, 2.622, 4.511, 8.639, and 9.572 keV, which are indicative of Cu, S, Cl, Ti, and Zn (Figure 36A). The LibLF ammunition was the only sample to show both S and Ti, along with the absence of Pb, Ba, and Sb in the spectral data.

This resulted in the LibLF having large negative scores. The FedLF sample also contained Ti, but with the absence of S, it resulted in having small negative scores, as opposed to the other lead-free samples which are not well described by this PC and thus obtain scores on the zero point of that PC.

The loadings plot for PC2 (Figure 36B) revealed a strong positive correlation at an energy of 1.740 keV, which is indicative of Si. Consequently, samples that show large positive scores on PC2, primarily those that contain LFP, contain substantial amounts of Si. Similarly, the loadings plot for PC2 revealed a strong negative correlation at energies 1.823, 3.605, 3.844, 3.954, 4.101, and 5.157 keV, which are indicative of Pb, Ba, and Sb (Figure 36B). Thus, samples that show large negative scores on PC2, primarily those that contain LBP, contain substantial amounts of Pb, Ba, and Sb. The LibLF ammunition shows negative scores for both PC1 and PC2 due to its primer showing a significantly different composition from both the LBP and LFP, i.e. the presence of S and Ti, and the absence of Pb, Ba, and Sb.

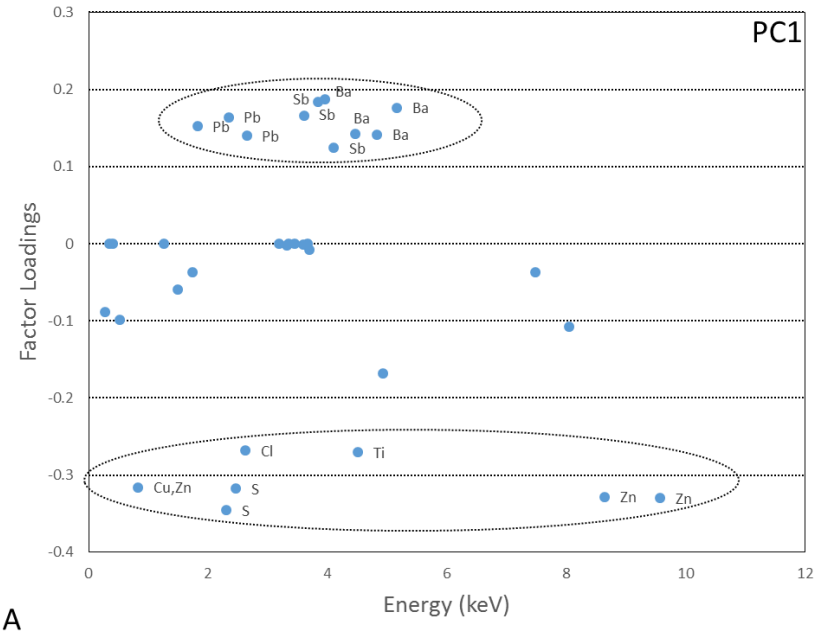


A

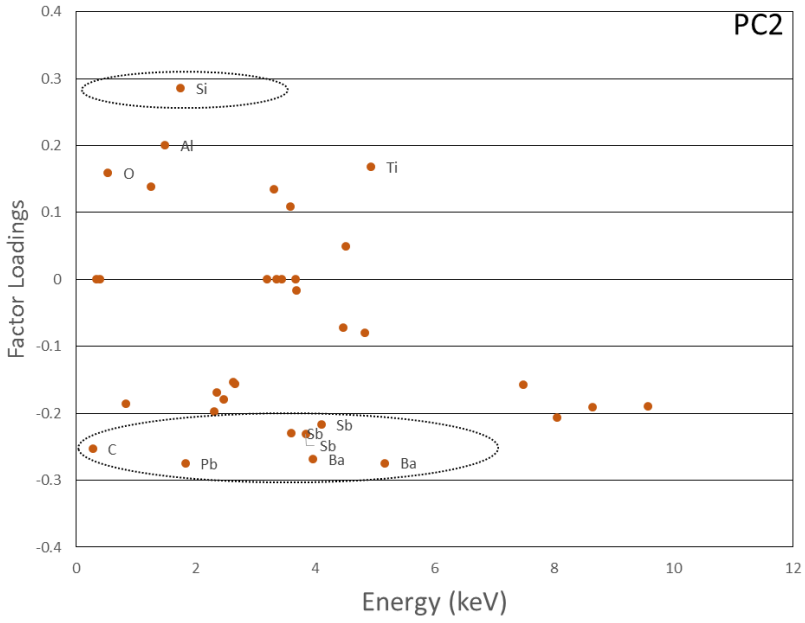


B

Figure 35: PCA scores plots, using the first three PCs A) shows the distribution of ammunition based on the LBP or LFP mixture B) shows the distribution of ammunition based on manufacturer



A



B

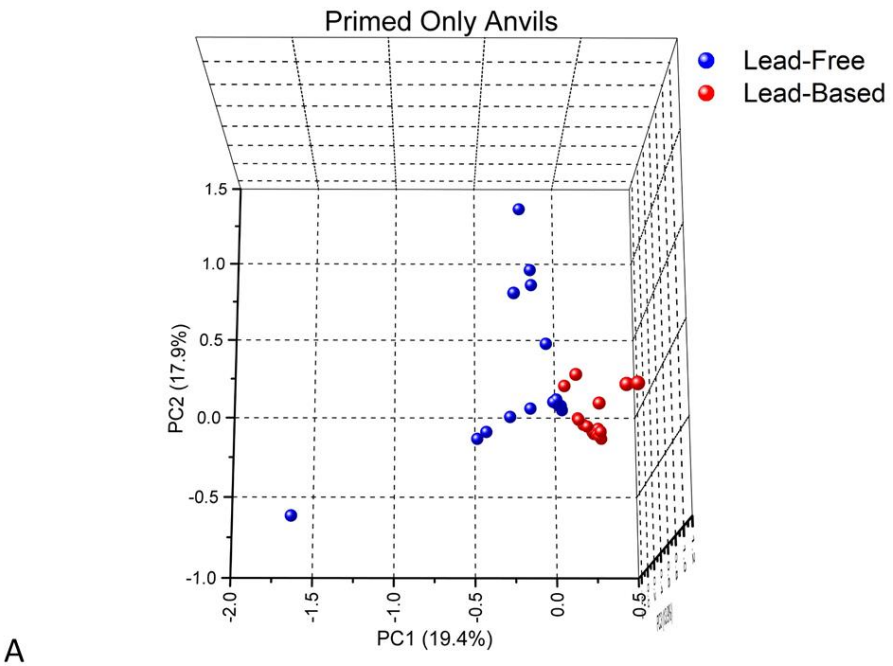
Figure 36: A) Factor loadings plot for PC1 B) Factor loadings plot for PC2

5.5.2 Primed Only Anvils

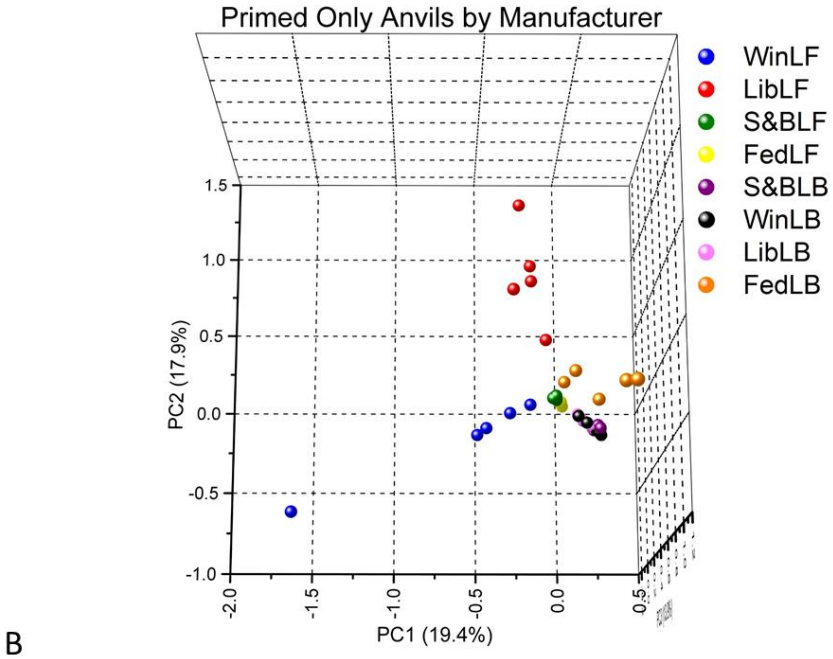
The PCA scores for the primed only anvils are illustrated in a three-dimensional plot in Figure 37. Figure 37A shows the separation of the ammunition based on the composition of its primer, i.e. LFP or LBP, and Figure 37B shows the separation of the ammunition based on the primer and the manufacturer. The factor loadings for the first two PCs can be examined to determine the elements that contributed to the variance (Figure 38). The loadings plot for PC1 (Figure 38A) showed strong positive correlations at energies 2.345, 2.605, 3.844, 4.466, and 4.828 keV, which are indicative of Pb, Ba, and Sb. Thus, samples that have large positive scores on PC1 (Figure 37) contain considerable amounts of Pb, Ba, and Sb, which in this dataset is LBP ammunitions. The loadings plot for PC1 also shows strong negative correlations at energies 3.314, 3.444, 3.590, and 3.666 keV, which are indicative of K and Sn. The WinLF sample contained both K and Sn in relatively high abundance resulting in this sample having relatively large negative scores on PC1. One sample of WinLF has a much higher negative score on PC1 than the other WinLF samples due to the intensities of the K and Sn being much lower in the EDX spectra (refer to Figure 32A). The S&BLF sample also contained K, but did not contain Sn, resulting in it having small negative scores on PC1, as opposed to the FedLF sample, which is at the zero point and is not well described by this PC.

The loadings plot for PC2 (Figure 38B) was examined, as well, and a strong positive correlation was revealed at energies 0.401, 0.832, 4.511, 4.932, and 8.639, which are indicative of Cu, Ti, and Zn. The LibLF sample showed large positive scores as a result of it being the only primed only sample to show Ti as a component of its residue. The plot also shows strong

negative correlations at energies 3.314, 3.444, 3.590, and 3.666 keV, which are indicative of K and Sn. Accordingly, the WinLF residue contained both K and Sn, resulting in it having relatively large negative scores on PC2. Similar to PC1, because the S&BLF samples contained K, but not Sn, the samples have small negative scores on PC2.

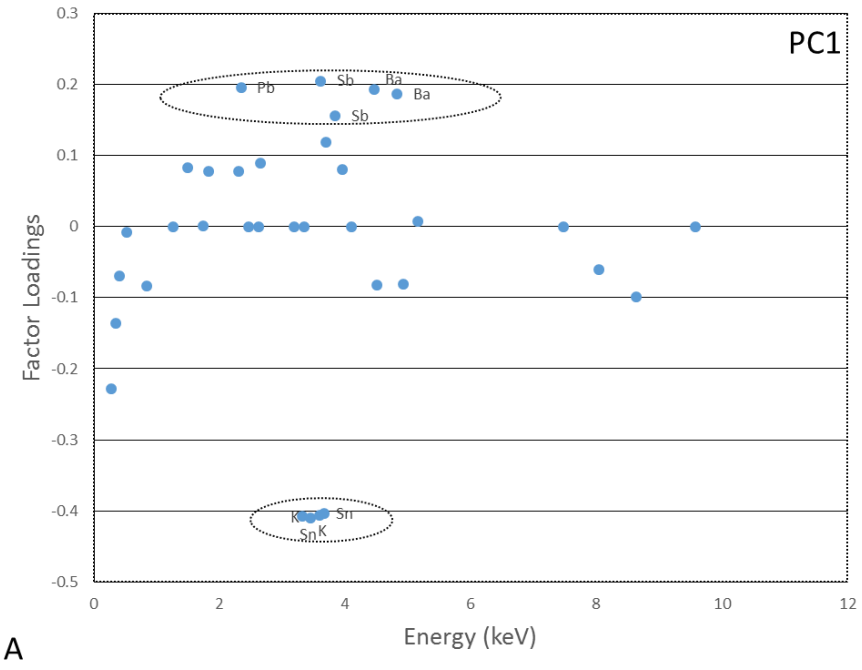


A

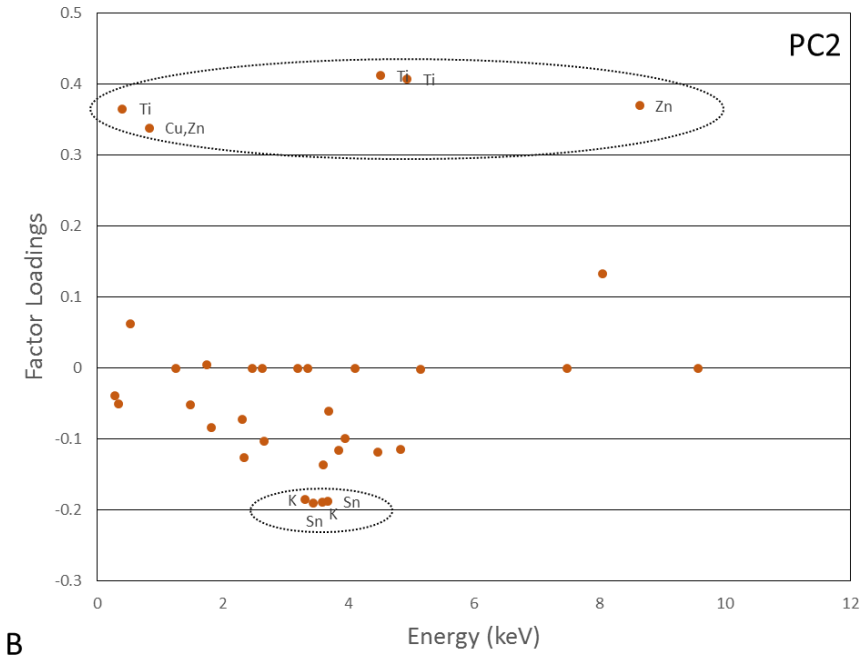


B

Figure 37: PCA scores plots, using the first three PCs A) shows the distribution of ammunition based on the LBP or LFP mixture B) shows the distribution of ammunition based on manufacturer



A



B

Figure 38: A) Factor loadings plot for PC1 B) Factor loadings plot for PC2

5.5.3 Full Cartridge Cups

Peaks of much lower intensity were collected for the cups, as opposed to the anvils, resulting in less separation of the samples. While the samples partially separated based on the priming mixture on PC1, the remaining PCs were more convoluted due to the elemental peaks becoming null once the data was processed to keep the peaks that met the LOD.

The PCA scores for the full cartridge cups are highlighted in three-dimensional plots in Figure 39 and Figure 40. Figure 39 shows the distribution of the ammunition on PC1, while Figure 40 shows the distribution on both PC2 and PC3. Figure 39A and Figure 40A show the distribution of ammunition based on the priming mixture, i.e. lead-based or lead-free. Figure 39B and Figure 40B show the distribution of ammunition based on both the primer and the manufacturer. The factor loadings can be studied from the first three PCs to determine the elements that contribute to the variance in the dataset (Figure 41). The loadings plot for PC1 (Figure 41A), shows strong positive correlations at energies of 1.254, 2.308, 2.464, and 2.622 keV, which are indicative of Mg, S, Cl, and Ti. Therefore, samples that have positive scores on PC1 contained trace amounts of these elements. Similarly, the loadings plot for PC1 also showed strong negative correlations at energies of 2.653, 3.844, 3.954, and 4.466 keV, which correspond to Pb, Ba, and Sb. Thus, samples that attain negative scores on PC1 contain considerable amounts of Pb, Ba, and Sb, primarily the lead-based ammunitions. The LibLB ammunition, however, did not contain Sb and, therefore, may not be well described by this PC, as it is at the zero point of the PC.

The loadings plot for PC2 (Figure 41B) was also analyzed and a strong positive correlation was noted at energies of 2.653, 3.844, 3.954, 4.466 keV, which are revealing of Pb, Ba, and Sb. Thus, samples which have positive scores on the PC2 showed peaks similar in energy that of Pb, Ba, and Sb. Likewise, the loadings plot revealed a strong negative correlation at an energy of 1.487 keV, which corresponds to Al. Those samples which have negative scores on PC2 contained peaks similar in energy to Al.

The loadings plot for PC3 (Figure 41C) showed a strong positive correlation at energies of 1.74 and 3.314 keV, which are indicative of Si and K, respectively. Thus, those samples which have positive scores on PC3, namely WinLF, showed peaks on the same energy as Si and K. Alternatively, those samples which showed Cu, Zn, and Al, which were common characteristics of most of the samples, have negative scores on PC3. This corresponds to the loadings plot for PC3, which shows strong negative correlations at energies of 0.832, 1.487, and 8.048 keV, which are indicative of Cu, Zn, and Al.

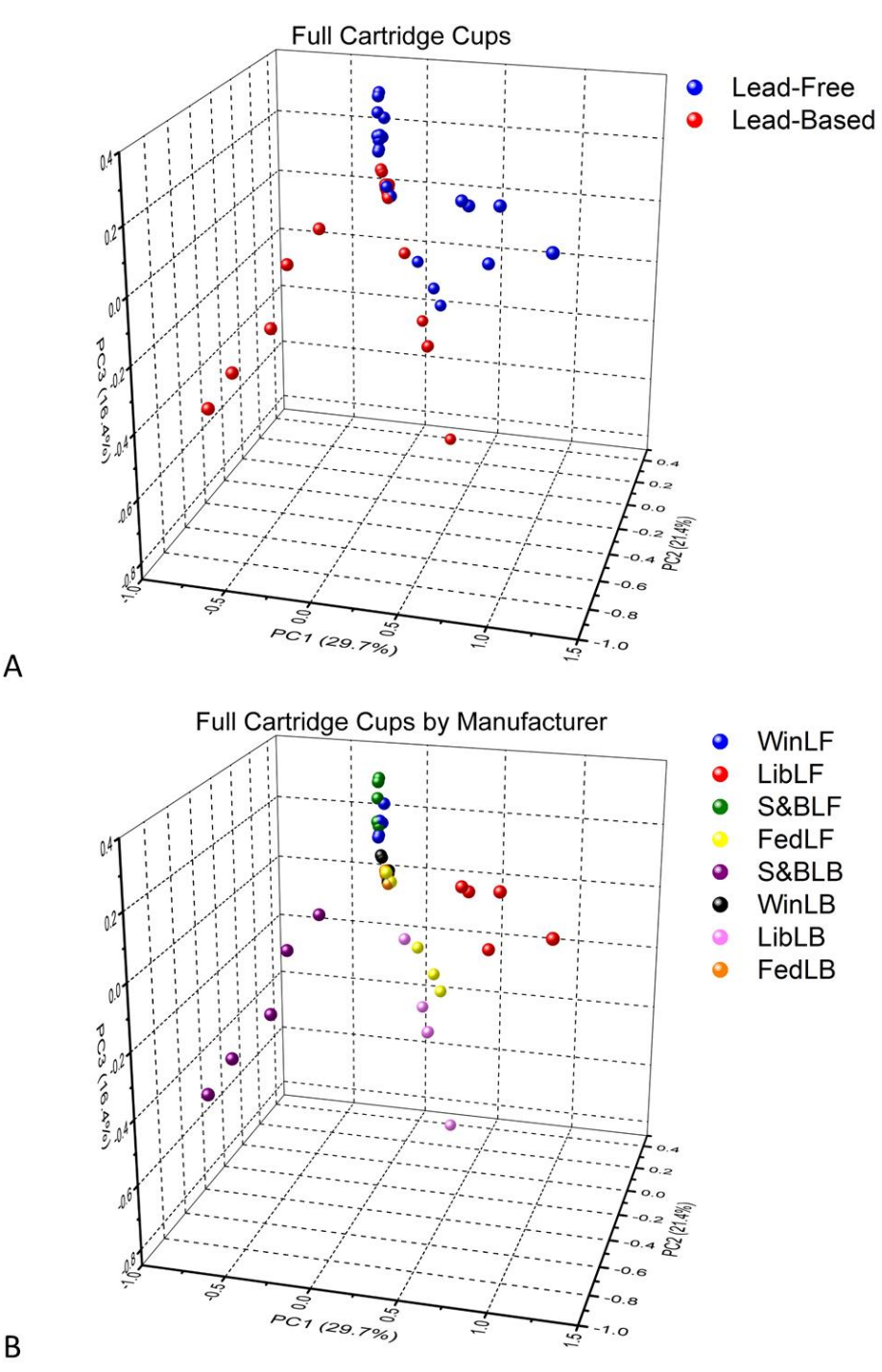
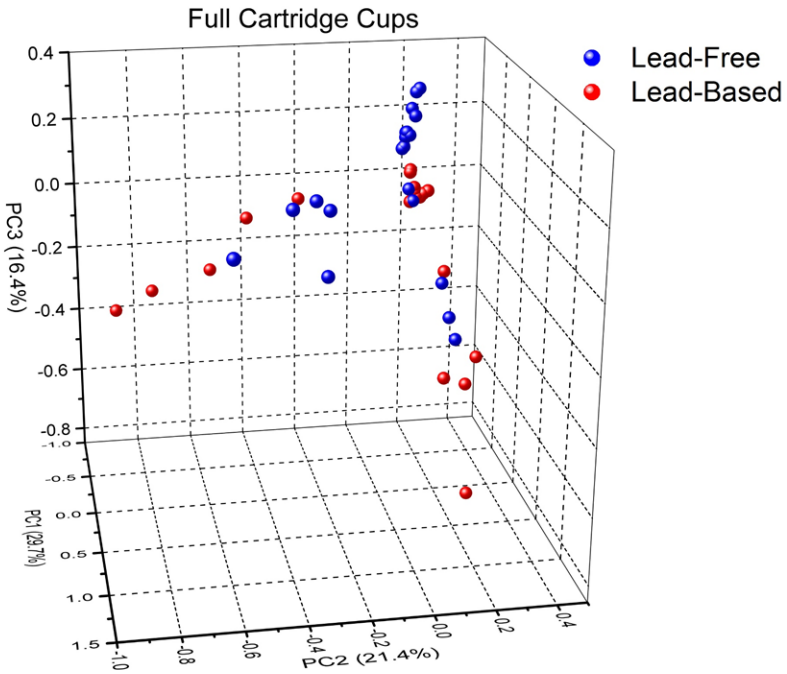


Figure 39: PC scores plot using the first three PCs, highlights the distribution of scores on PC1 A) PC scores plot by the priming mixture, i.e. lead-based or lead-free B) PC scores plot by manufacturer

A



B

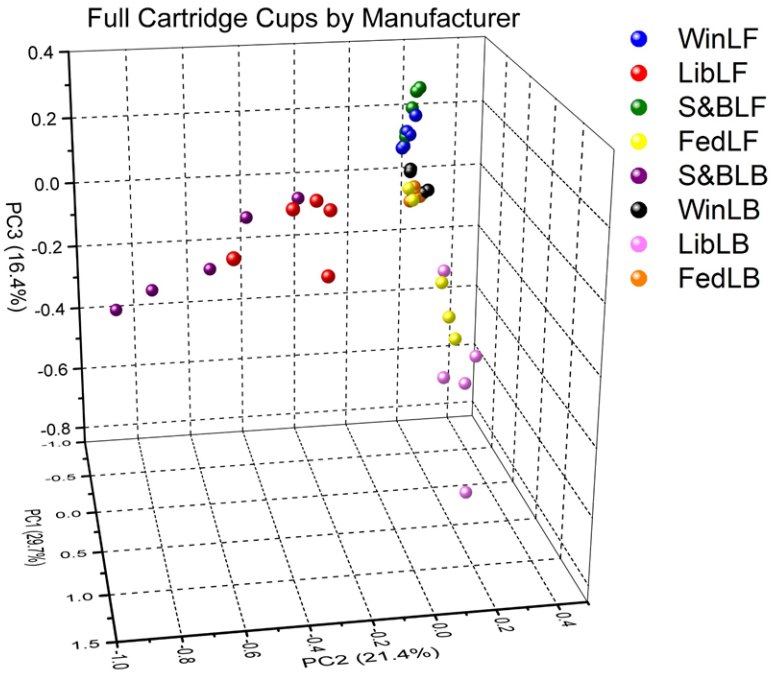
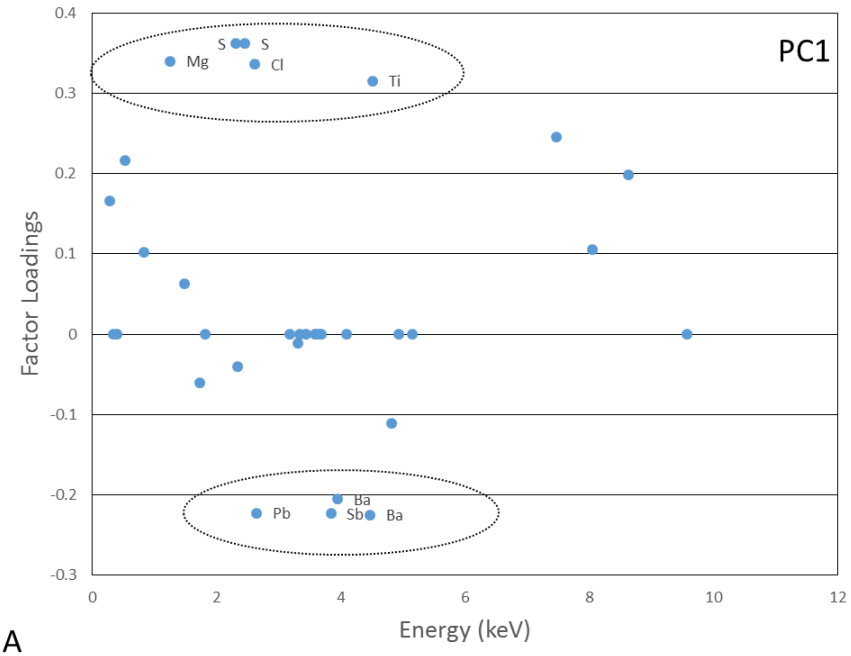
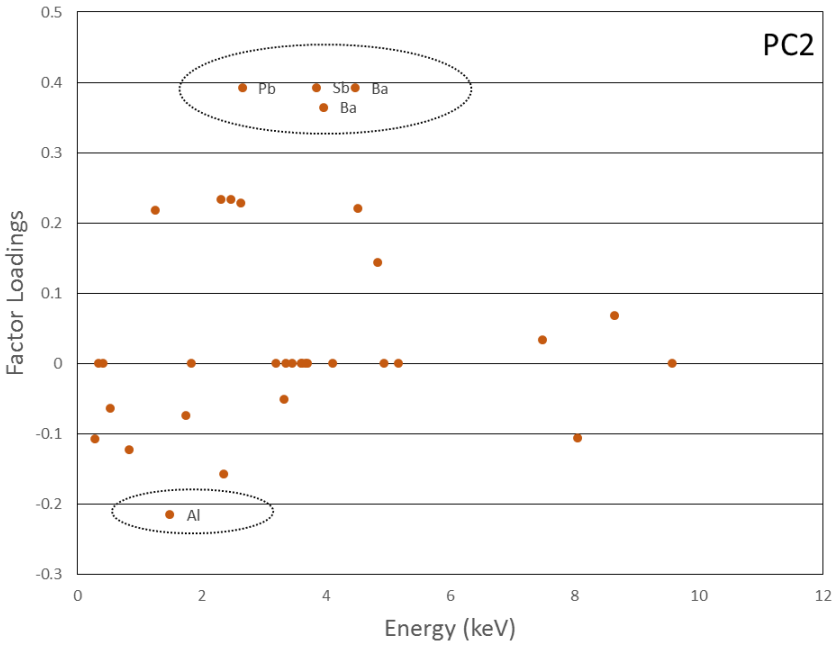


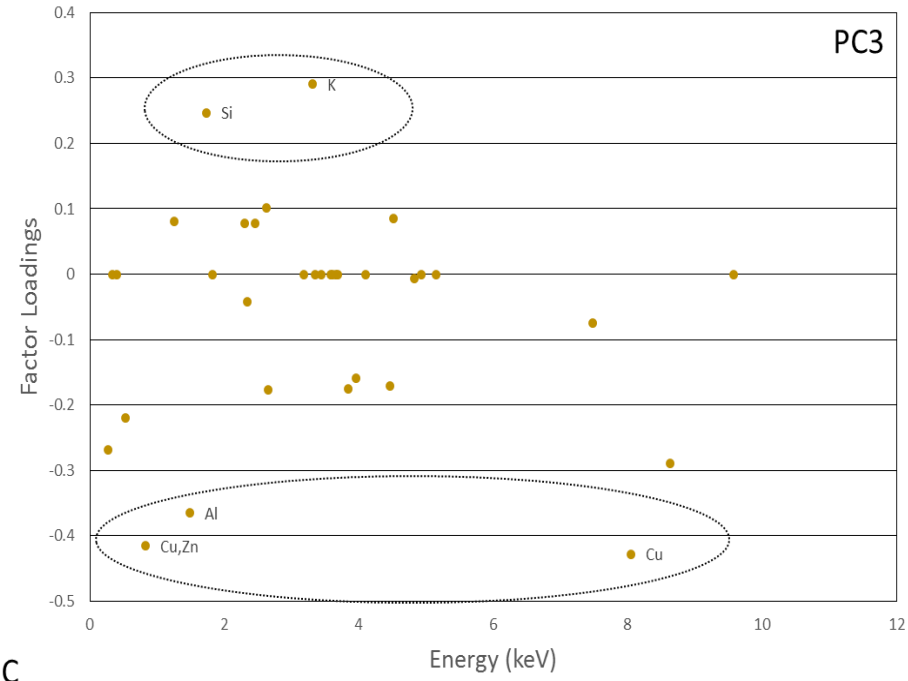
Figure 40: PC scores plots using the first three PCs, highlights the distribution of scores on PC2 and PC3 A) PC scores plot by the priming mixture, i.e. lead-bead or lead-free B) PC scores plot by manufacturer


PC1
Factor Loadings
Energy (keV)
S
S
Mg
Cl
Ti
Ba
Pb
Sb
Ba
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
0
2
4
6
8
10
12

A


PC2
Factor Loadings
Energy (keV)
Pb
Sb
Ba
Ba
Al
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
0
2
4
6
8
10
12

B



C

Figure 41: A) Factor loadings for PC1 B) Factor loadings for PC2 C) Factor loadings for PC3

5.5.4 Primed Only Cups

When full cartridge ammunition is discharged, the smokeless powder provides back pressure within the cartridge which causes the majority of the primer residue to remain within the priming cup after detonation. With the absence of smokeless powder in the primed only cartridges, the majority of the primer residue exits the muzzle of the weapon, leaving very little behind to analyze. As a result, finding particles to analyze was difficult, and the subsequent spectra showed less characterization than previous datasets.

The PCA scores for the primed only cups are illustrated in three-dimensional plots in Figure 42 and Figure 43. Figure 42 shows the distribution of ammunition on PC1 with Figure 42A showing the distribution according to the priming mixture, and Figure 42B showing the

distribution based on the manufacturer. Similarly, Figure 43 shows the distribution of ammunition on PC2 and PC3, with Figure 43B showing the two different distributions. Looking at the loadings for PC1 (Figure 44A), there is a slight positive correlation at energies of 0.341, 0.401, 0.832, and 1.740, which correspond to Ca, Ti, Cu, Zn, and Si. Thus, those samples which showed peaks of energies consistent to these elements have positive scores on PC1. Due to the low intensities of the peaks for these samples, this results in the majority of the ammunition being characterized by this PC, except for the WinLF. Similarly, a slight negative correlation is present at energies of 1.823, 2.308, 2.653 , and 3.844 keV, which are indicative of Pb, Ba, and Sb. While these are typically indicative of a lead-based primer, the absence, or small intensities, of these in the majority of the primed only cups resulted in them not having negative scores on PC1.

The loadings for PC2 and PC3 (Figure 44B and Figure 44C, respectively) can also be analyzed to find characteristics to differentiate between the ammunitions. The loadings for PC2 show strong positive correlations at energies of 1.74, 3.314, and 3.692 keV, which are indicative of Si, K, and Ca. The loadings also showed negative correlations at energies of 0.341, 4.466, and 4.828, which correspond to Ca and Ba. Thus, samples which have positive scores on PC2 showed energies corresponding Si, K, and 3.692 keV peak Ca, while those with negative scores on PC2 showed energies corresponding to the 0.341 peak for Ca, and Ba.

The loadings for PC3 showed strong positive correlations at energies of 1.74, 3.314, and 3.692 keV, which correspond to Si, K, and Ca, such as the loadings for PC2 show. The loadings also show a negative correlation at energies of 0.401, 7.478, 8.639 keV, which are indicative of

Ti, Ni, and Zn. Only one sample out of the whole dataset had positive scores on PC3. The majority of the samples having negative scores on PC3 is to be expected as Si, K, and Ca did not often show peaks of high enough intensity to be deemed significant, and Zn and Ni are present as a component of most of the priming cups.

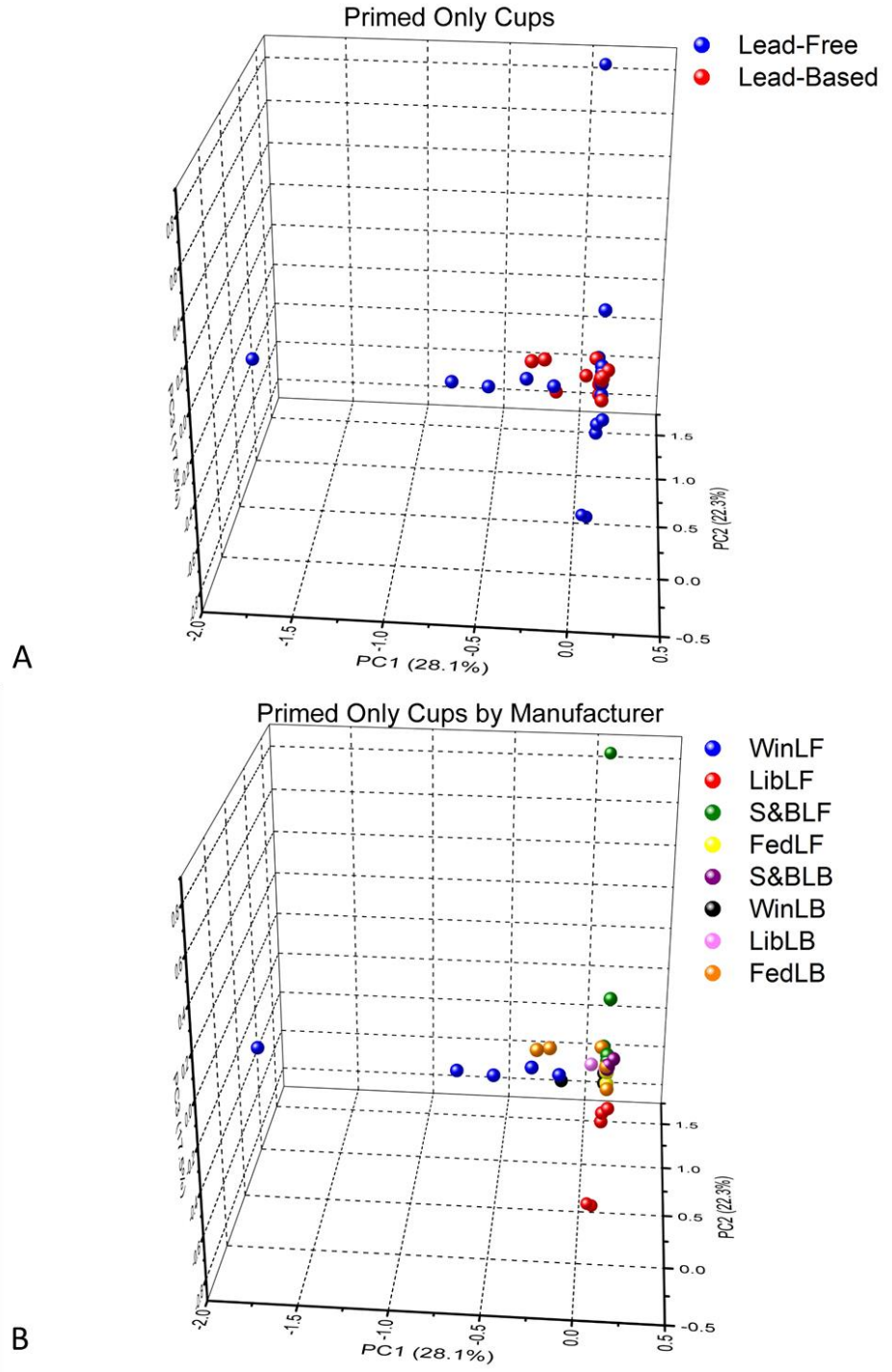
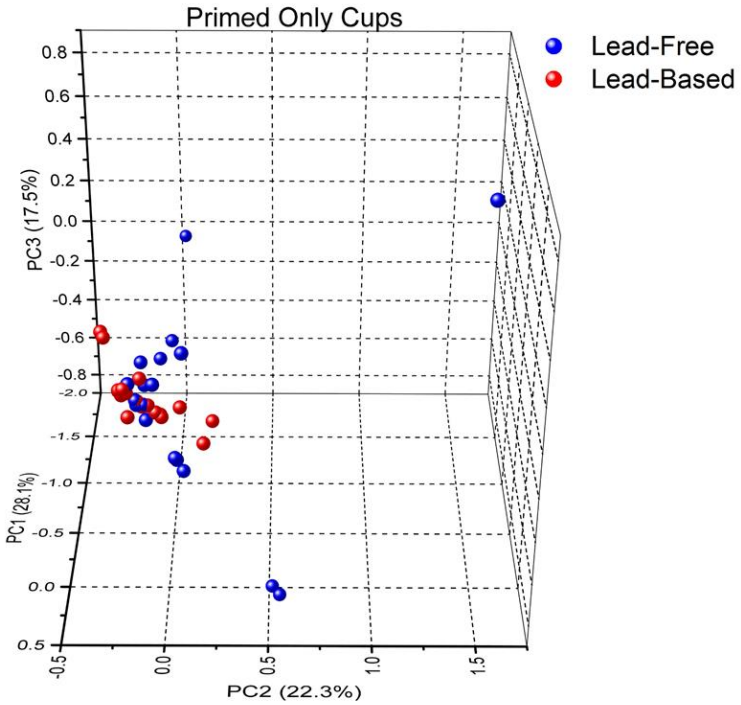


Figure 42: PC scores plot using the first three PCs, highlights the distribution of scores on PC1 A) PC scores plot by the priming mixture, i.e. lead-based or lead-free B) PC scores plot by manufacturer

A



B

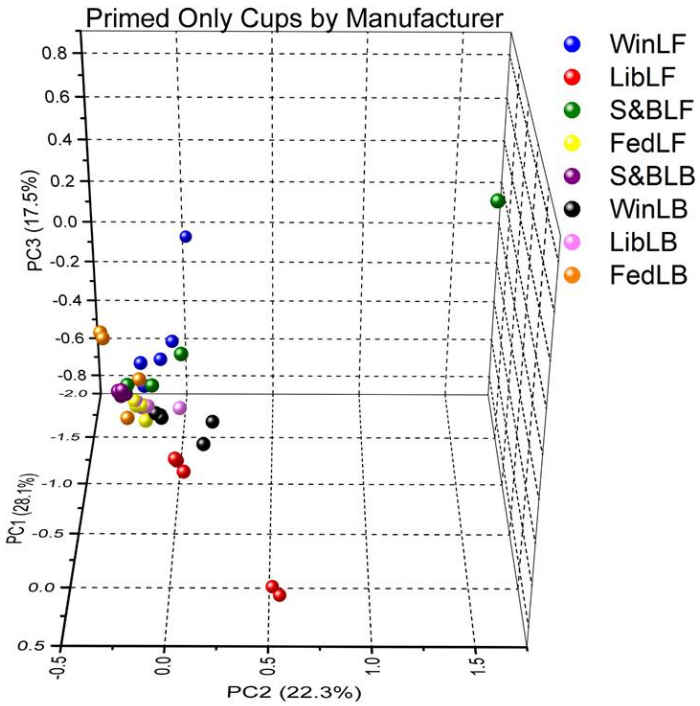
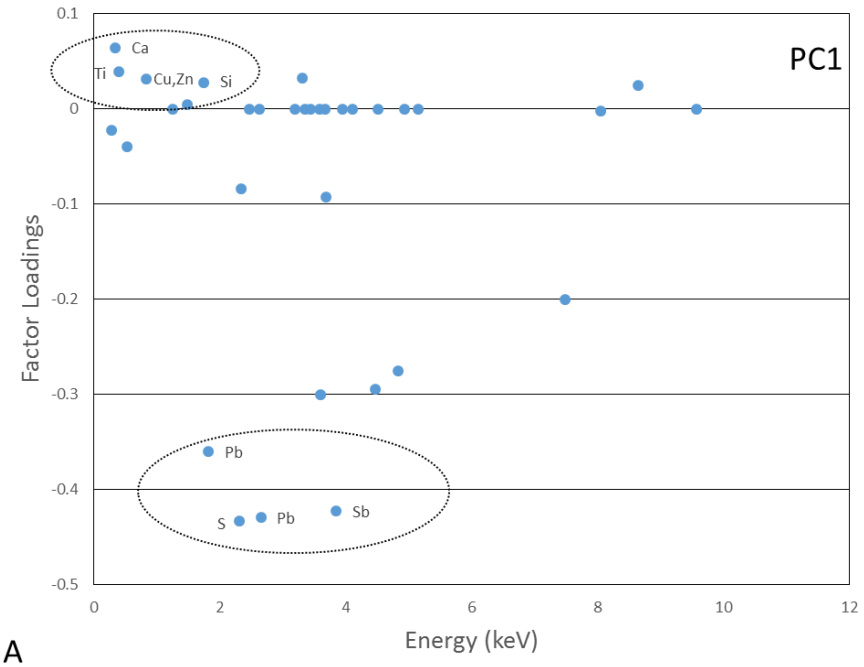
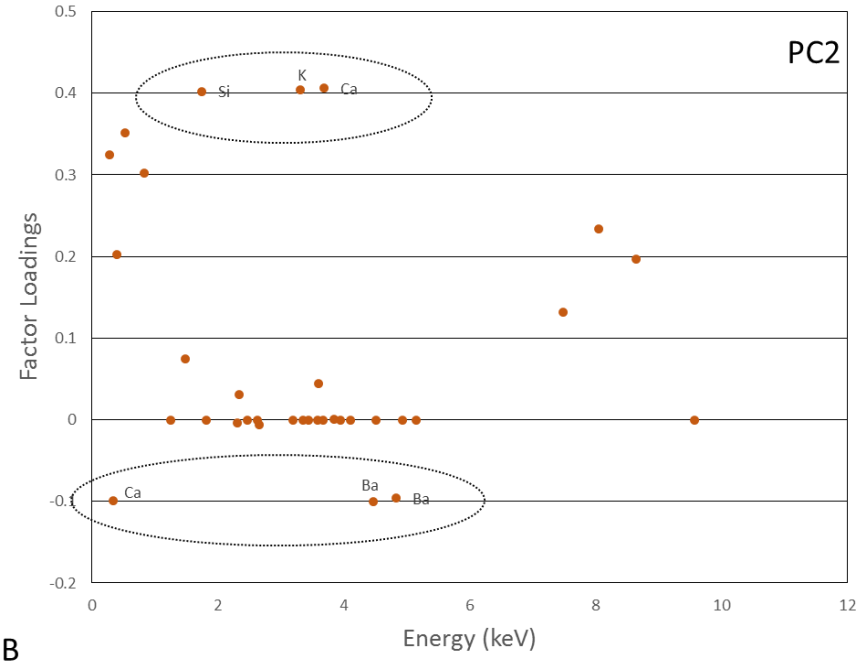


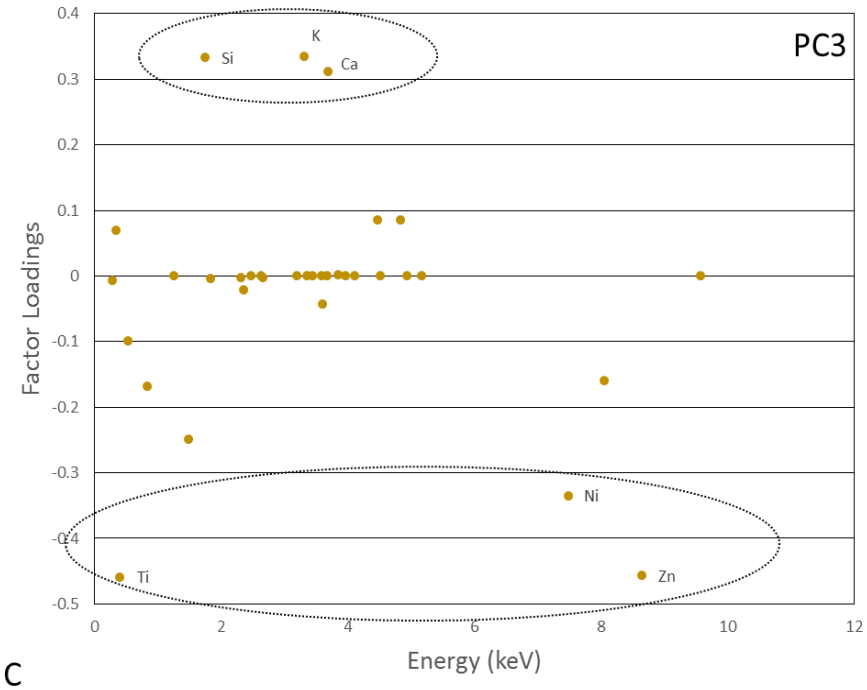
Figure 43: PC scores plots using the first three PCs, highlights the distribution of scores on PC2 and PC3 A) PC scores plot by the priming mixture, i.e. lead-bead or lead-free B) PC scores plot by manufacturer


PC1
Factor Loadings
Energy (keV)
Ca
Ti
Cu,Zn
Si
Pb
S
Pb
Sb
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
2
4
6
8
10
12

A


PC2
Factor Loadings
Energy (keV)
K
Si
Ca
Ca
Ba
Ba
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
0
2
4
6
8
10
12

B



C

Figure 44: A) Factor loadings for PC1 B) Factor loadings for PC2 C) Factor loadings for PC3

5.6 Linear Discriminant Analysis

LDA was performed using the first nine PC scores (~90% of the variance) for both the full cartridge and primed only anvils, as well as a combined matrix of the two datasets. A 5-fold cross-validation was done on the datasets which was then repeated ten times. This resulted in 400 samples each for the full and primed only datasets and 800 samples for the combined matrix. The actual classifications against the predicted classifications can be seen in the confusion matrices in Figure 45, along with the total number of samples and the percent correctly classified. Figure 45A shows the results for the full cartridge anvils which showed 100% of objects classified correctly. The primed only anvils are represented in Figure 45B and

shows 99.8% of objects correctly classified, while the combined matrix resulted in 97.5% of objects correctly classified (Figure 45C).

A second test set of priming residue, from ammunitions not used in the models, was used to test the classification of the LDA model. Fourteen LBP and three LFP samples from four different manufacturers were collected and used as the 'test set' for the model. The test set was tested against each model created using the model (Figure 45) and the results are summarized in the confusion matrices in Figure 46. The first matrix (Figure 46A) shows the test set against the full cartridge anvils which resulted in nine of the LBP samples and two of the LFP samples classifying correctly to give 64.7% of objects correctly classified. Figure 46B shows the test set against the primed only anvils which showed five LBP and two LFP samples classifying correctly, which resulted in 41.1% of the samples classifying correctly. The test set compared to the full and primed only combined matrix is shown in Figure 46C. The percentage of correctly classified objects is identical to that of the full cartridge model; however, the classifications are distributed differently with eight of the LBP classified correctly and all three of the LFP classified correctly. A larger test set with a greater number of LFP samples might provide a better indication of the classification capabilities of the model.

A LDA for the Full Cartridge Anvils

		Actual			
		LBP	LFP	Total	% Correct
Predicted	LBP	**200**	0	**200**	**100**
	LFP	0	**200**	**200**	**100**
	Total	**200**	**200**	**400**	**100**

B LDA for the Primed Only Anvils

		Actual			
		LBP	LFP	Total	% Correct
Predicted	LBP	**200**	**1**	**201**	**99.5**
	LFP	0	**199**	**199**	**100**
	Total	**200**	**200**	**400**	**99.8**

C LDA for the Full Cartridge and Primed Only Anvils Combined Matrix

		Actual			
		LBP	LFP	Total	% Correct
Predicted	LBP	**389**	**9**	**398**	**97.7**
	LFP	**11**	**391**	**402**	**98.6**
	Total	**400**	**400**	**800**	**97.5**

Figure 45: Confusion matrices summarizing assignments of the samples classified with 5-fold cross-validation LDA for A) the full cartridge anvils B) primed only anvils C) and a combined matrix of the full and primed only cartridge datasets

A LDA for the Full Cartridge Anvils with Secondary Test Set

Predicted	Actual: LBP	Actual: LFP	Actual: Total	% Correct
LBP	**9**	**1**	**10**	**90**
LFP	**5**	**2**	**7**	**28.6**
Total	**14**	**3**	**17**	**64.7**

B LDA for the Primed Only Anvils with Secondary Test Set

Predicted	Actual: LBP	Actual: LFP	Actual: Total	% Correct
LBP	**5**	**1**	**6**	**83.3**
LFP	**9**	**2**	**11**	**18.2**
Total	**14**	**3**	**17**	**41.1**

C LDA for the Full and Primed Only Combined Matrix with Secondary Test Set

Predicted	Actual: LBP	Actual: LFP	Actual: Total	% Correct
LBP	**8**	0	**8**	**100**
LFP	**6**	**3**	**9**	**33.3**
Total	**14**	**3**	**17**	**64.7**

Figure 46: Confusion matrices of the samples classified based on the previously created models for A) the full cartridge anvils B) the primed only anvils C) and the combined matrix of the full and primed only cartridge datasets

5.7 Muzzle Discharge Residue

5.7.1 EDX Spectra

The follow results show the EDX spectra for the two types of ammunition which were chosen for muzzle discharge analysis. The residue was collected on a cotton cloth target and then stubbed using aluminum mounts with carbon adhesive tape. Each sample was scanned in its entirety, and then three particles were chosen for individual spot scans. The resulting EDX are showcased against the spectra from the anvils of the same ammunition.

Analysis of the Sellier & Bellot LFP full cartridge muzzle discharge residue showed similar EDX characteristics to that of the anvils (Figure 47A). Si was present in all five of the residues collected from the full cartridge anvils, and, subsequently, Si was detected in two of the three individual particles chosen for analysis. A notable difference between the two is the absence of K in the muzzle discharge and addition of Ca in one of the spectra. While Ca was not detected on the full cartridge anvils, there were peaks of low intensity for the primed only anvils. However, Ca was not detected in the primed only muzzle discharge (Figure 47B). Nevertheless, the absence of Pb, Ba, and Sb, and the addition of Si and Ca, does provide consistent characteristics with LFP ammunition.

Conversely, the analysis of the Winchester LBP full cartridge muzzle discharge residue (Figure 48A) showed very few similarities with that of the respective anvils. While the spectra did show the presence of Sb, which is consistent with LBP, the peaks for Pb are so small as to be almost negligible. One particle, however, did show the presence of Ba, which was detected on the anvils. The primed only muzzle discharge samples, though, did show more similar

characteristics to that of the anvils (Figure 48B). Pb was present in three of the four spectra, Sb was present in one of the particles analyzed, and Ba was present in two of the particles. The presence of Pb, Ba, and Sb, while scarce, does show characteristics with LBP ammunition.

Overall, the muzzle discharge does show some similarities to its respective primer residue, however, a larger set of muzzle discharge residue would be ideal to further showcase the connection between them. The samples used for this analysis were a small subset of a much larger sample set of all of the ammunitions used. Nonetheless, these two ammunitions provide a visual representative of the two different primer compositions outlined in this research.

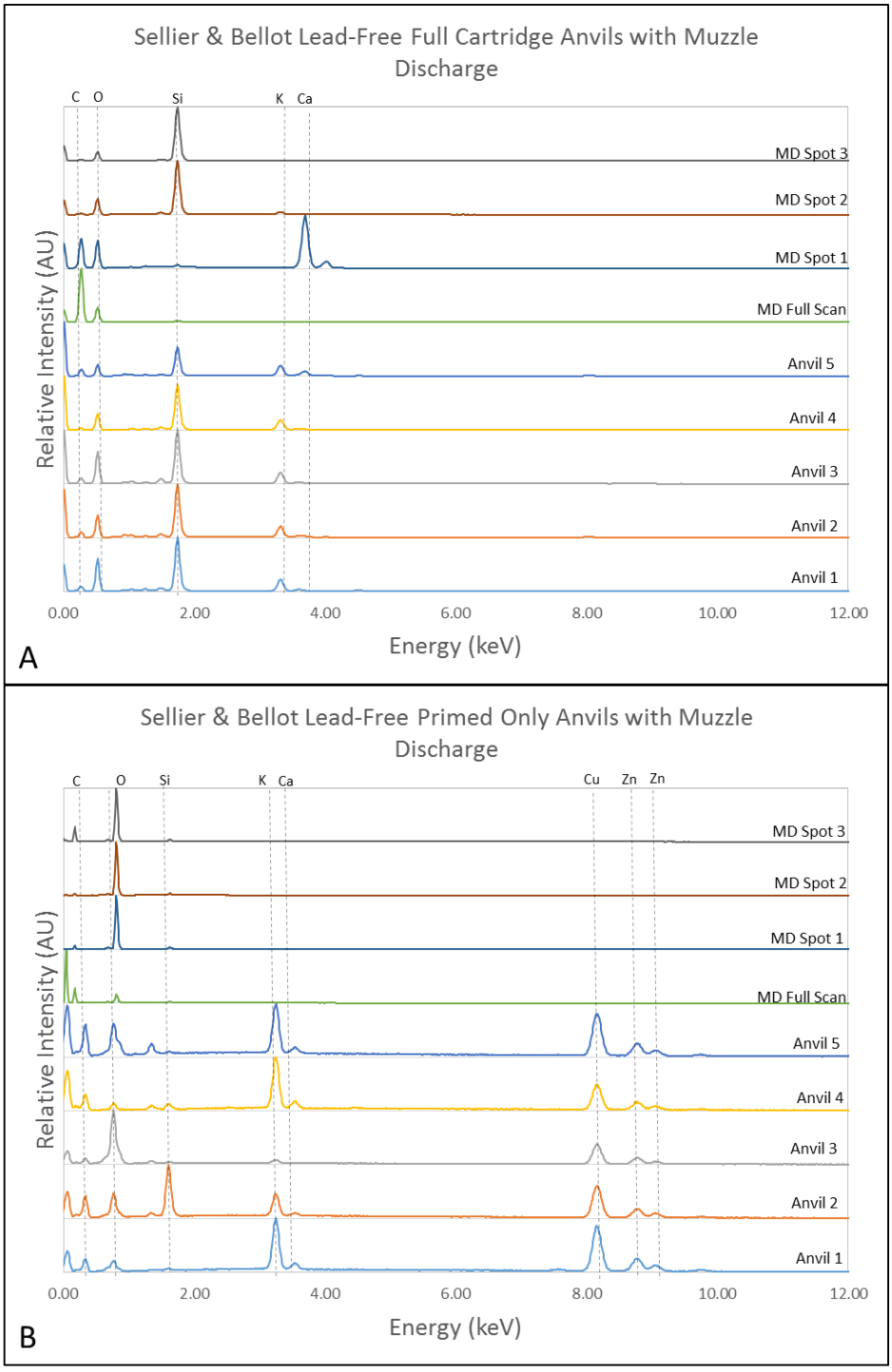


Figure 47: A) Sellier & Bellot lead-free full cartridge anvils with muzzle discharge B) Sellier & Bellot lead-free primed only anvils with muzzle discharge.

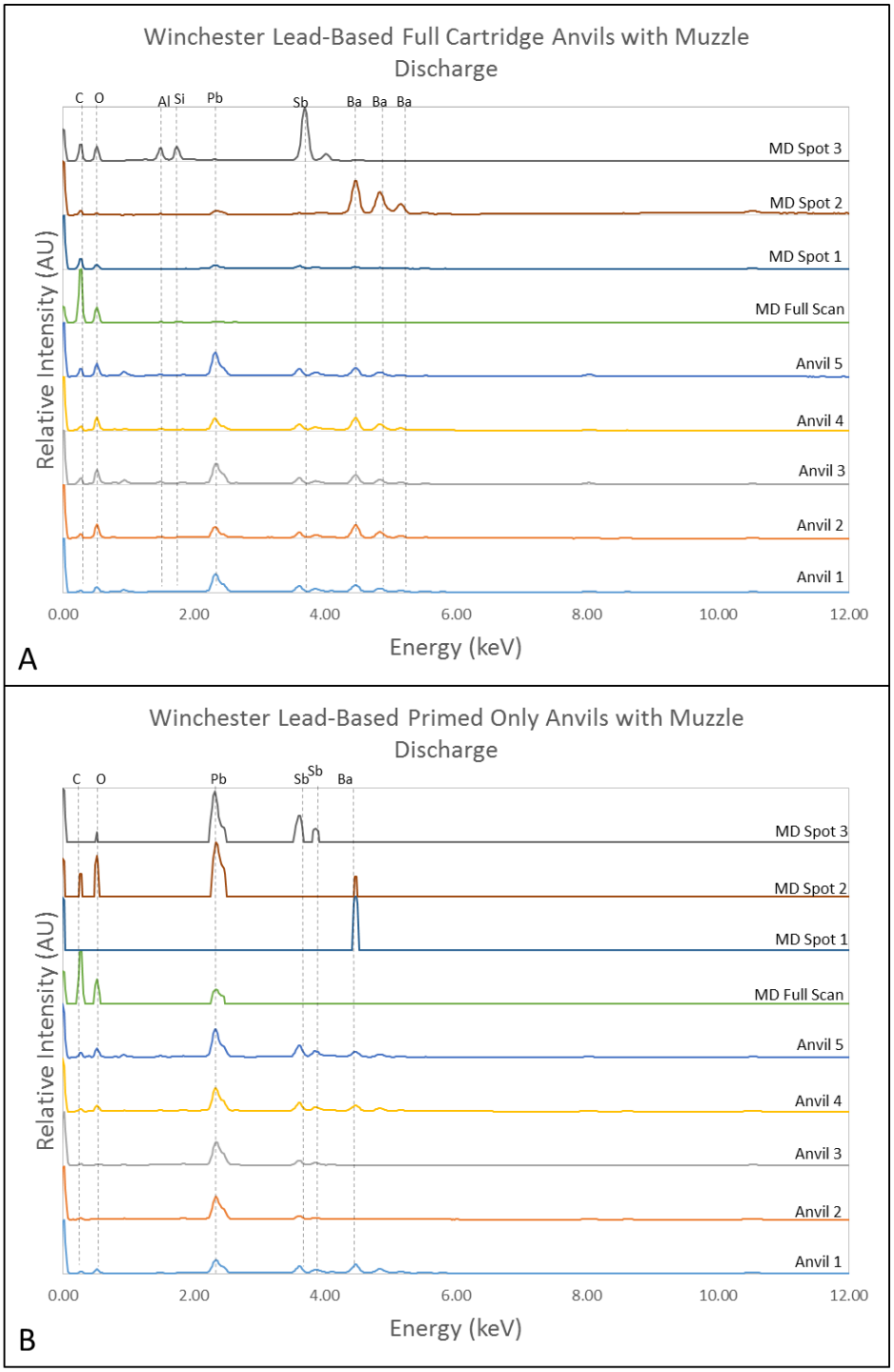


Figure 48: A) Winchester lead-based full cartridge anvils with muzzle discharge. B) Winchester lead-based primed only anvils with muzzle discharge.

5.7.2 Principal Component Analysis

In addition to the EDX spectra, PCA was also performed for the muzzle discharge residue in order to generate three-dimensional PC scores plots of the muzzle residue against the residue collected from the full and primed only anvils (Figure 49). The factor loadings for the first two PCs are presented in Figure 50 and can be used to determine the elements which caused variance in the dataset.

Looking at the scores plot for the full cartridge anvils (Figure 49A) and the respective loadings for PC1 (Figure 50A), a strong positive correlation can be seen at energies of 1.823, 2.345, 2.653, 3.605, 3.844, 3.954, 4.101, 4.466, 4.828, 5.157 keV, which correspond to Pb, S, Ba, and Sb. Thus, samples that have large positive scores on PC1 (refer to Figure 49A), primarily the LBP ammunitions, contain Pb, Ba, and Sb. Only one of the lead-based muzzle discharge samples showed significant peaks for Sb, and only one showed peaks for Ba, while none of them showed major peaks for Pb. This results in the majority of the lead-based muzzle discharge samples lying close to the zero point of the PC, similar to the lead-free muzzle discharge samples which are absent of these three components. Due to the absence of the three elements characteristic of LBP ammunitions in both sets of muzzle discharge, the majority of the samples lie within the lead-free range along PC1.

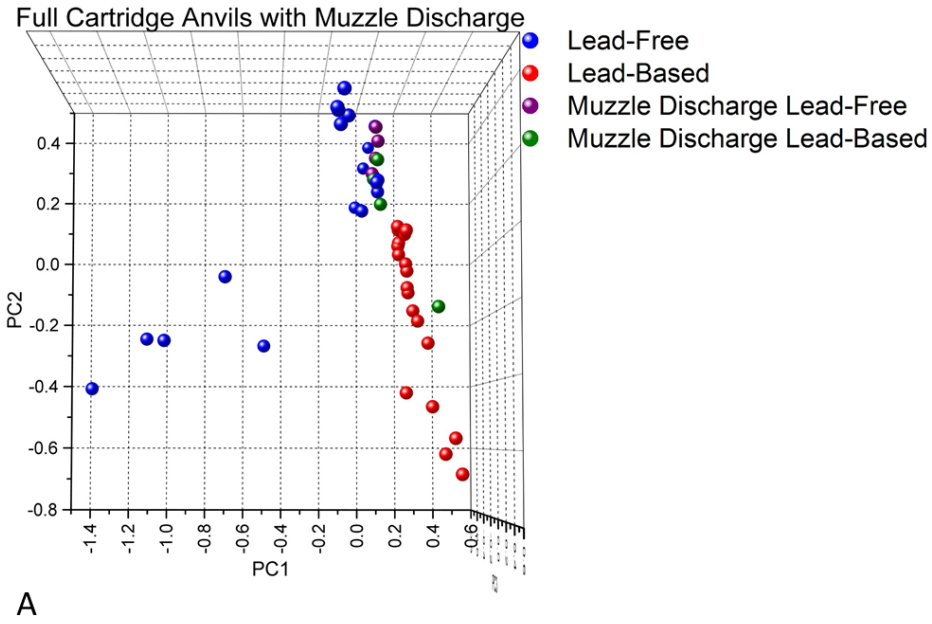
Similarly the loadings plot for PC2 (Figure 50B) showed strong positive correlations at energies of 0.525, 1.487, 1.74, and 3.314 keV, which are indicative of O, Al, Si, and K. Two of the four lead-free muzzle discharge samples have significant peaks for Si which resulted in those samples having large positive scores on PC2 (Figure 49A). Si and K are typically characteristics of

LFP ammunition, and thus those samples which had peaks for these elements show characteristics with LFP along PC2. The loadings plot also showed strong negative correlations at energies of 1.823, 3.605, 3.844, and 3.954 keV, which correspond to Pb, Sb, and Ba. Consequently, those samples which have negative scores on PC2 contain Pb, Sb, and Ba. The muzzle discharge only showed Sb and Ba for one sample, and, thus, the majority of the samples lie within the lead-free range on PC2.

This method was also utilized for the primed only samples, which appear to show more correlation to their corresponding primer mixtures (Figure 49B). The factor loadings can further be examined to determine the elements which contributed to the variance (Figure 51). The loadings plot for PC1 (Figure 51A) showed strong positive correlations at energies of 1.823, 2.308, 2.345, 2.653, 3.605, 3.692, 3.954, 4.466, and 4.8285 keV, which are indicative of Pb, S, Ba, and Sb. Samples that show large positive scores on PC1, primarily the the LBP ammunitions, contain Pb, Ba, and Sb. Three of the four lead-based muzzle discharge samples contained significant peaks for Pb, and, thus, these samples have positive scores on PC1. This results in them clustering primarily with the LBP ammunition. The lead-free primed only muzzle discharge samples did not show significant peaks consistent either the LBP or LFP, and, thus, their scores on PC1 lie close to the zero point of the PC.

The loadings plot for PC2 (Figure 51B) shows strong positive correlations at energies of 0.401, 0.832, 4.511, 4.932, and 8.639 keV, which correspond to Ti, Cu, and Zn. The muzzle discharge samples did not contain Ti for the either the LBP or LFP, and, thus, neither show positive scores on PC2. The loadings plot showed strong negative scores at energies of 1.823,

2.308, 2.345, 2.653, 3.605, 3.844, 3.954, 4.466, and 4.828 keV, which are indicative of Pb, S, Ba, and Sb. Three of the LBP muzzle discharge did have those components characteristic of LBP ammunition and, therefore, those samples have negative scores on PC2.



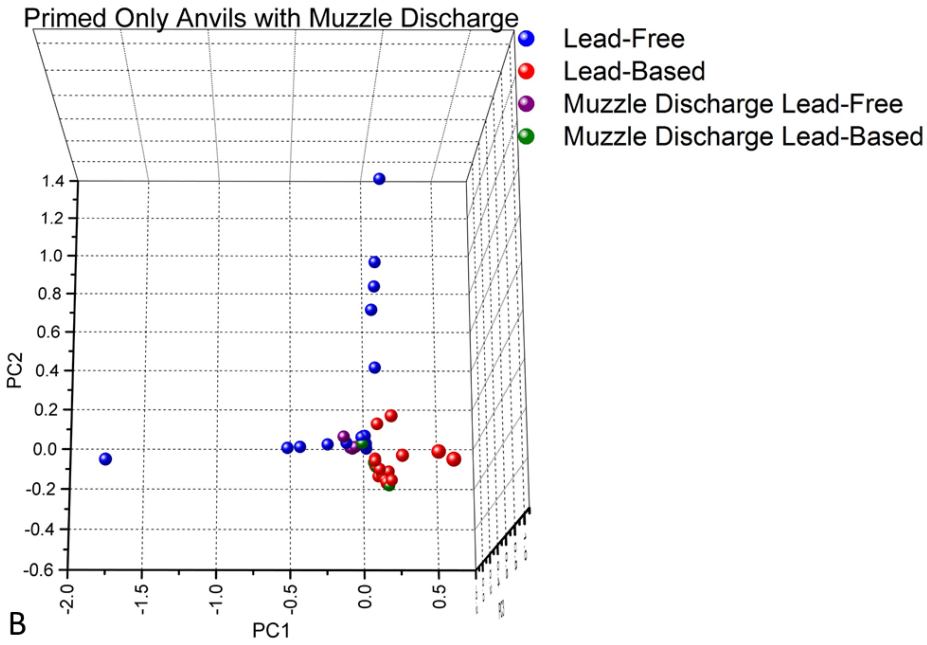


Figure 49: PC scores plot using the first three PCs, highlights the distribution of anvils against the muzzle discharge residue A) PC scores plot for the full cartridge ammunition B) PC scores plot for the primed only ammunitions

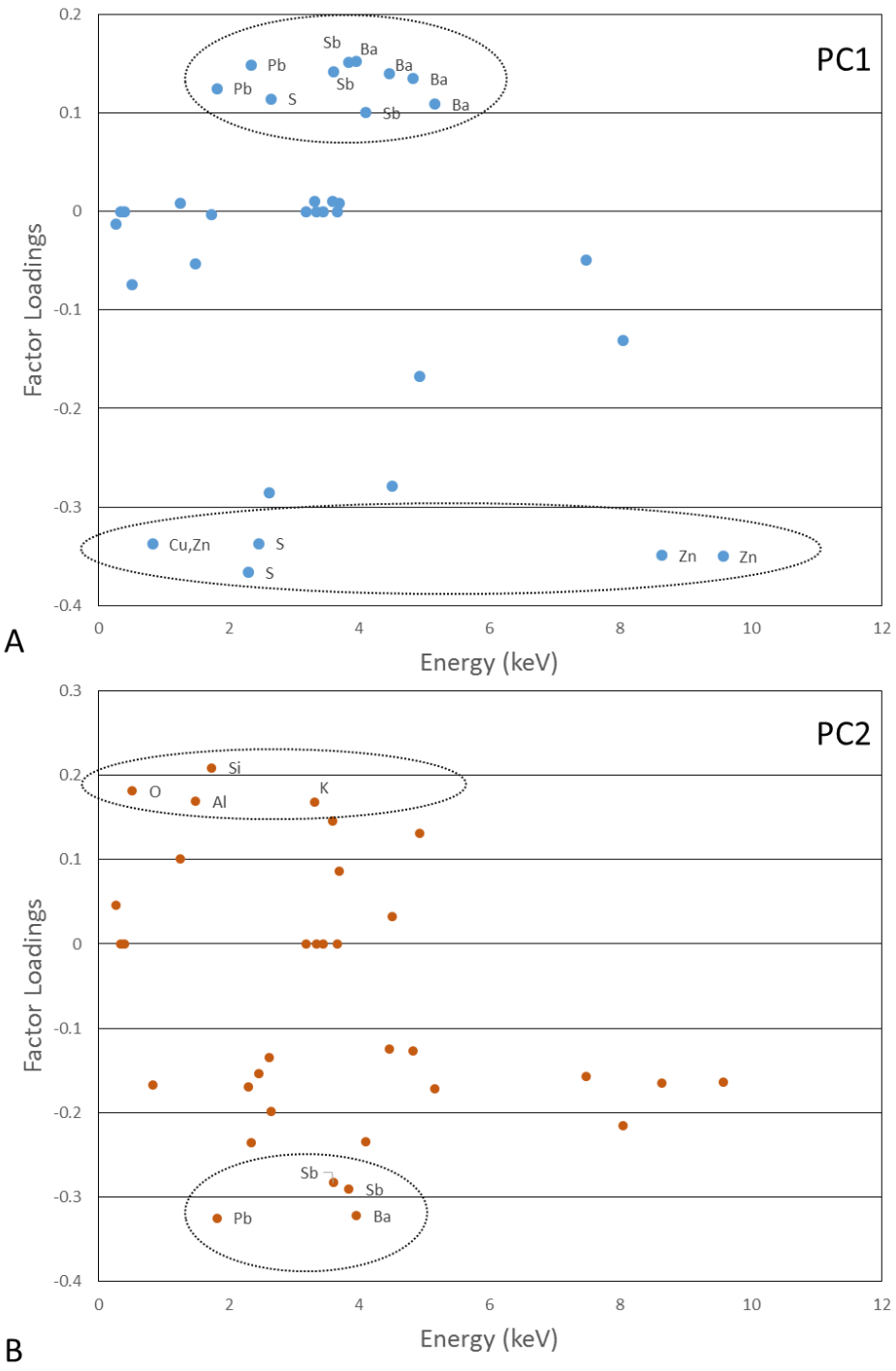


Figure 50: Factor loadings for the full cartridge anvils with muzzle discharge A) Factor loadings for PC1 B) Factor loadings for PC2

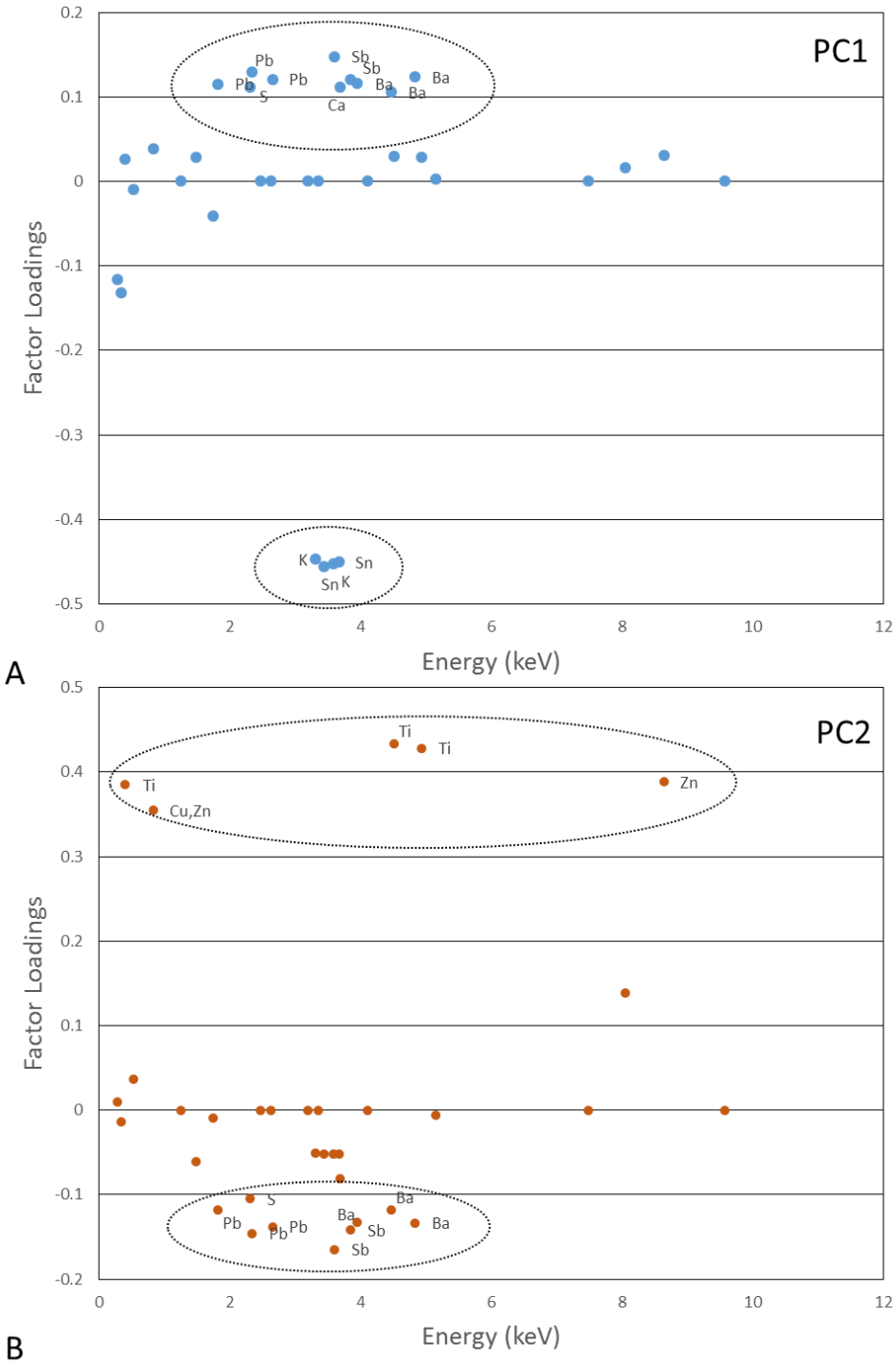


Figure 51: Factor loadings for the primed only anvils with muzzle discharge A) Factor loadings for PC1 B) Factor loadings for PC2

CHAPTER 6: CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The goals of this research project were to develop a method of distinguishing GSR apart from the traditional methods in order to develop a method of characterization between lead-based and lead-free ammunition. This was done by determining the physical and chemical differences between LBP and LFP residue, as well as the components of the cartridge case, i.e. the priming cup, which can contribute to GSR. The research presented showed the elemental components of eight different ammunitions, four LBP and four LFP, using SEM-EDX accompanied by PCA for statistical analysis. The ammunitions were fired as both full and primed only cartridges and the resulting post-fire cartridges were collected for analysis. The priming cups, and subsequently the anvils, were removed and five of each were adhered to aluminum stubs. Three spectra were collected from each cup and anvil, and the spectra were averaged to generate a single spectra per anvil or cup. The spectra were then normalized using the maximum peak and LOD, and condensed into four graphs per ammunition, i.e. full cartridge anvils, full cartridge cups, primed only anvils, and primed only cups. The spectral data was condensed by picking out the peaks corresponding to the energies of specific elements, normalized using unit vector analysis with sum of squares, and used for PCA and LDA.

The EDX spectra for each ammunition were compared to the MSDSs provided by the manufacturers in order to determine the origin of the elements present in the residue. The majority of the samples showed consistencies with their respective MSDSs, except for the lead-

free Liberty sample, which had so little information provided that it was incomparable to the residue. Three elements which were often found in the residue but were not present in any of the MSDSs were Al, Si, and Ti. Al was present in many of the LBP and LFP samples and may be present as either a fuel or frictionator. Similarly, Si was present in three of the four LFP samples, Si can be used in conjunction with calcium to act as either a fuel or frictionator. Ti was also present in three of the four LFP ammunitions, but did not appear in any of the MSDSs, however it may be added as a replacement, or in addition to, calcium silicide.

One characteristic of the priming cup was the presence of Ni in the residue of those cups which are Ni plated. Another priming cup characteristic was the presence of Cu and Zn in the majority of the spectra, both LBP and LFP, due to the brass composition of the priming cup and anvil. Pb, Ba, and Sb are the elements characteristic of TGSR, which was consistent in that none of the LFP samples showed Pb or Sb, and only one of them, the Federal lead-free, showed peaks for Ba. K was present in two of the four lead-free samples due to the barium nitrate being replaced, which is common is toxic metal free primers, with potassium nitrate.

Along with the analysis of the EDX spectra, the spectral data was used to perform PCA to determine whether the ammunitions would cluster based on both the primer mixture and manufacturer. It was determined that the anvils provided a better dataset due to the difficulty in collecting X-rays from the priming cups and, thus, provide better characterization and separation of the samples. While some separation was present in the full cartridge cups, the data from the primed only cups was too convoluted to provide accurate interpretations. The

anvils, however, provided separation both by the primer composition, i.e. LBP or LFP, and by manufacturer.

In addition to the PC scores plots, LDA was run using the PCA scores from the full cartridge and primed only anvils using the percent withheld method. Eighty percent of the datasets were used as the training set to create the LDA model, and the remaining twenty percent were used as the test sets to determine whether the model could correctly classify samples. For both the full cartridge and primed only anvils, all eight samples withheld for testing correctly classified as either LFP or LBP. A secondary dataset containing anvils of ammunitions not used in this research was used in place of the test set to determine the classification rate of the LDA model. Eleven of the seventeen samples classified correctly resulting in 64.7% correctly classified object. Eight of the fourteen LBP samples classified correctly, while all three LFP samples were correctly identified.

Lastly, two samples (the S&BLF and WinLB) were chosen for analyzing the muzzle discharge residue. Both the full and primed only cartridges were discharged at cotton targets and the residue was collected using an aluminum stub with carbon adhesive tape. The samples were analyzed via SEM-EDX, and the resulting spectral data was analyzed via PCA and compared to the PCA for the full and primed only anvils. When compared to the full cartridge anvils, the samples both clustered within the lead-free region, while the primed only anvils appeared to separate more by their primer composition. This may be a result of the primed only cartridges having more primer residue present on the target due to the absence of the smokeless powder. When the smokeless powder is present there is a pressure created that

pushes back on the primer mixture resulting in much of it remaining behind in the priming cup. Without the smokeless powder, the majority of the primer travels through the flash hole and exits the muzzle of the weapon.

6.2 Future Work

This research focuses on a fairly small subset of ammunition manufacturers, and as such, only provides a small window of information that could be gained from the analysis of primer residue. With that in mind, future work might include the expansion of the amount of ammunition samples used to more thoroughly encompass the amount of ammunition readily available. While a definitive distinction is made between the LFP and LBP, a larger set of samples which incorporates more manufacturers may provide a better idea of whether the ammunition is classifiable by manufacturer, as opposed to its primer composition.

Secondly, while the information presented provides an LDA model suitable for comparing against itself and another small subset of data, a larger set of samples to test against the LDA model might provide a better indication of the classification ability of ammunition. In addition to that, more muzzle discharge samples would be necessary to relate the primer residue back to the residue which is typically found after a shooting. This would further verify the origin of characteristic components of GSR and determine whether it is classifiable by the same means. This may ultimately provide a secondary method of identifying GSR, apart from the traditional methods outlined by ASTM, and offer a means of linking a suspect to a shooting.

APPENDIX A: ELEMENTAL ENERGIES

Peak Energy	Element
0.277	C
0.341	Ca
0.401	Ti
0.525	O
0.832	Cu,Zn
1.254	Mg
1.487	Al
1.740	Si
1.828	Pb
2.308	S
2.345	Pb
2.464	S
2.653	Pb
2.622	Cl
3.189	Sb
3.314	K
3.347	Sb
3.444	Sn
3.590	K
3.605	Sb
3.666	Sn
3.692	Ca
3.844	Sb
3.954	Ba
4.101	Sb
4.511	Ti
4.466	Ba
4.828	Ba
4.932	Ti
5.157	Ba
7.478	Ni
8.048	Cu
8.639	Zn
9.572	Zn

APPENDIX B: SEM IMAGES ANVILS AND CUPS

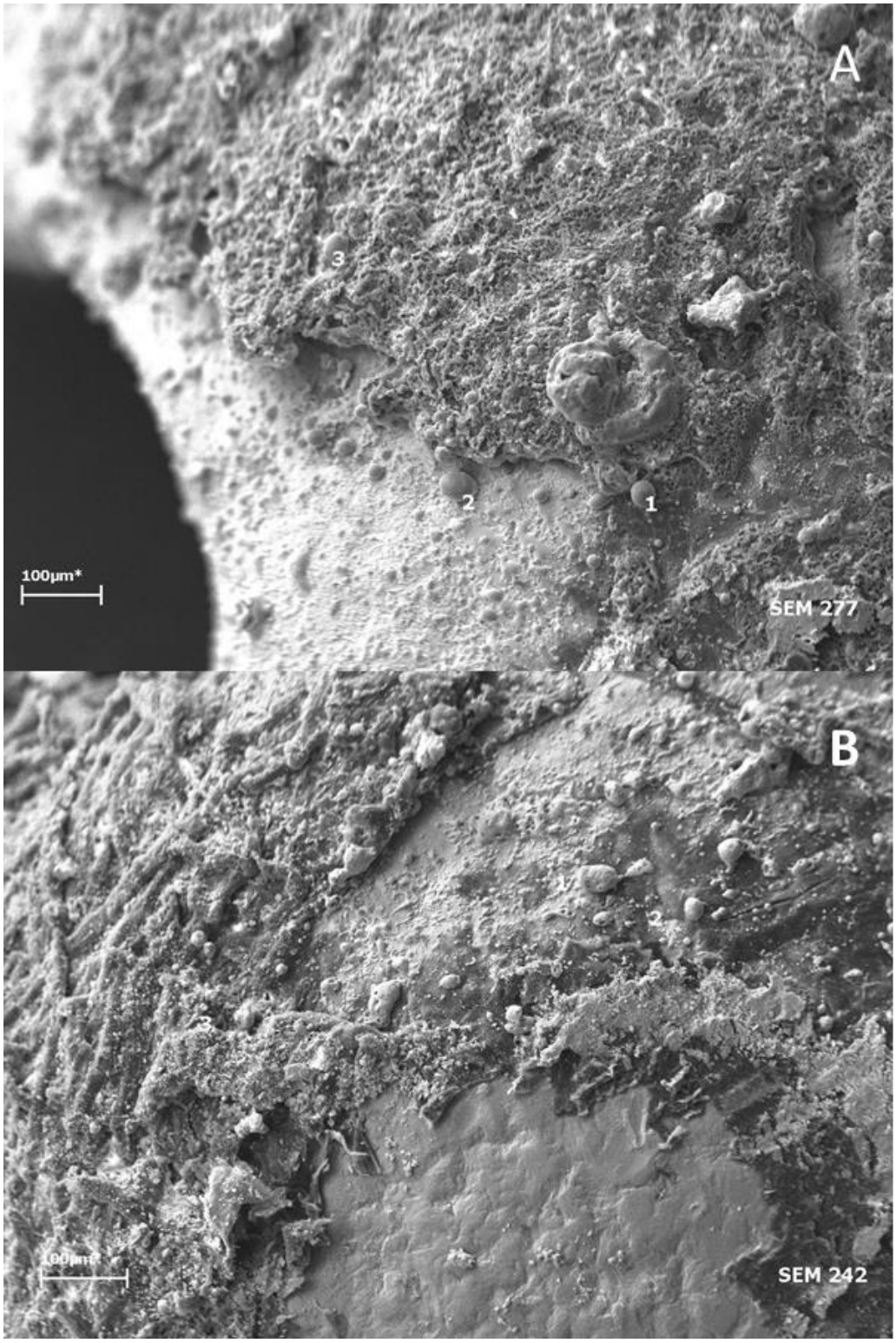


Figure 52: Federal Lead-Based Anvils A) Full Cartridge B) Primed Only

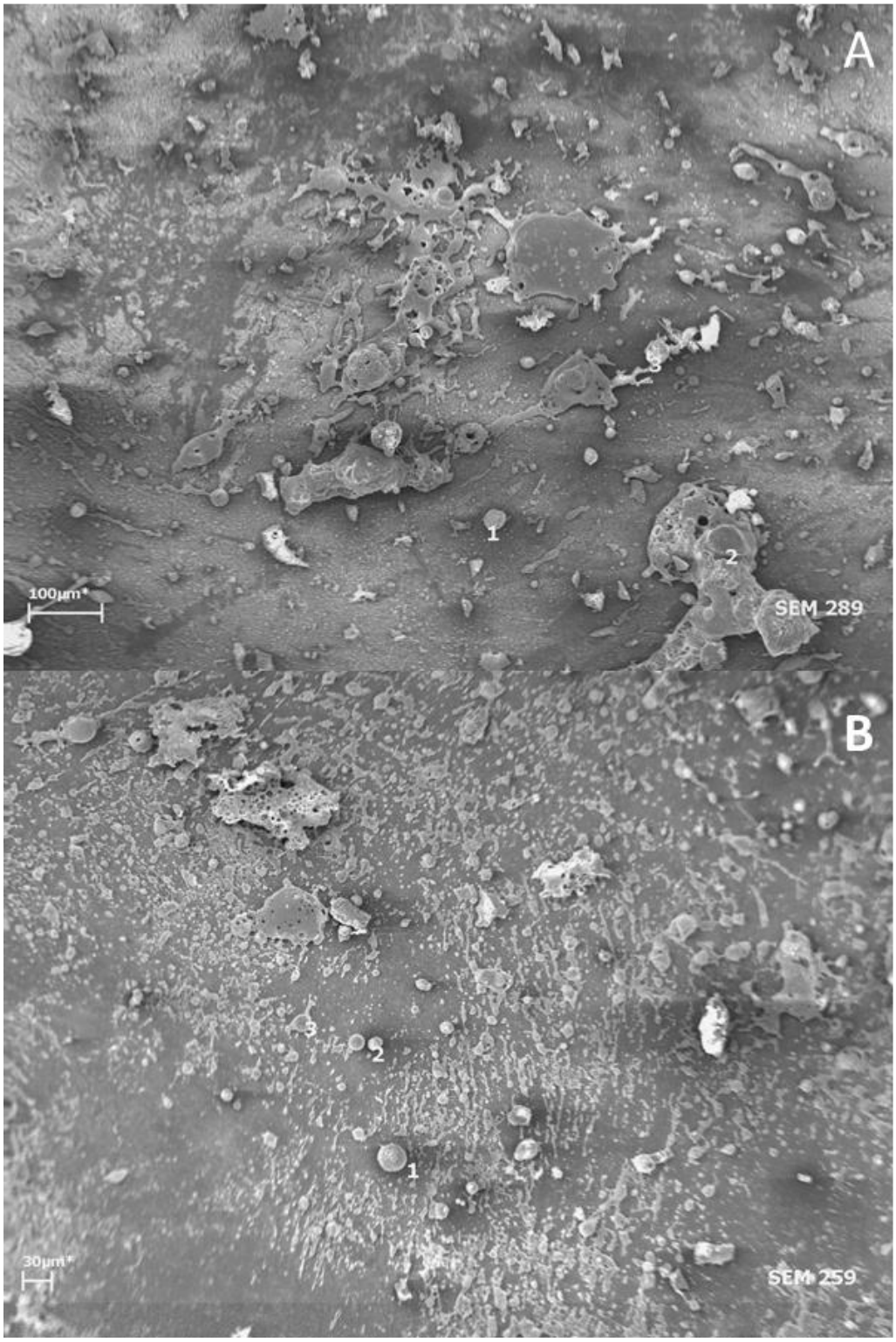


Figure 53: Federal Lead-Based Cups A) Full Cartridge B) Primed Only

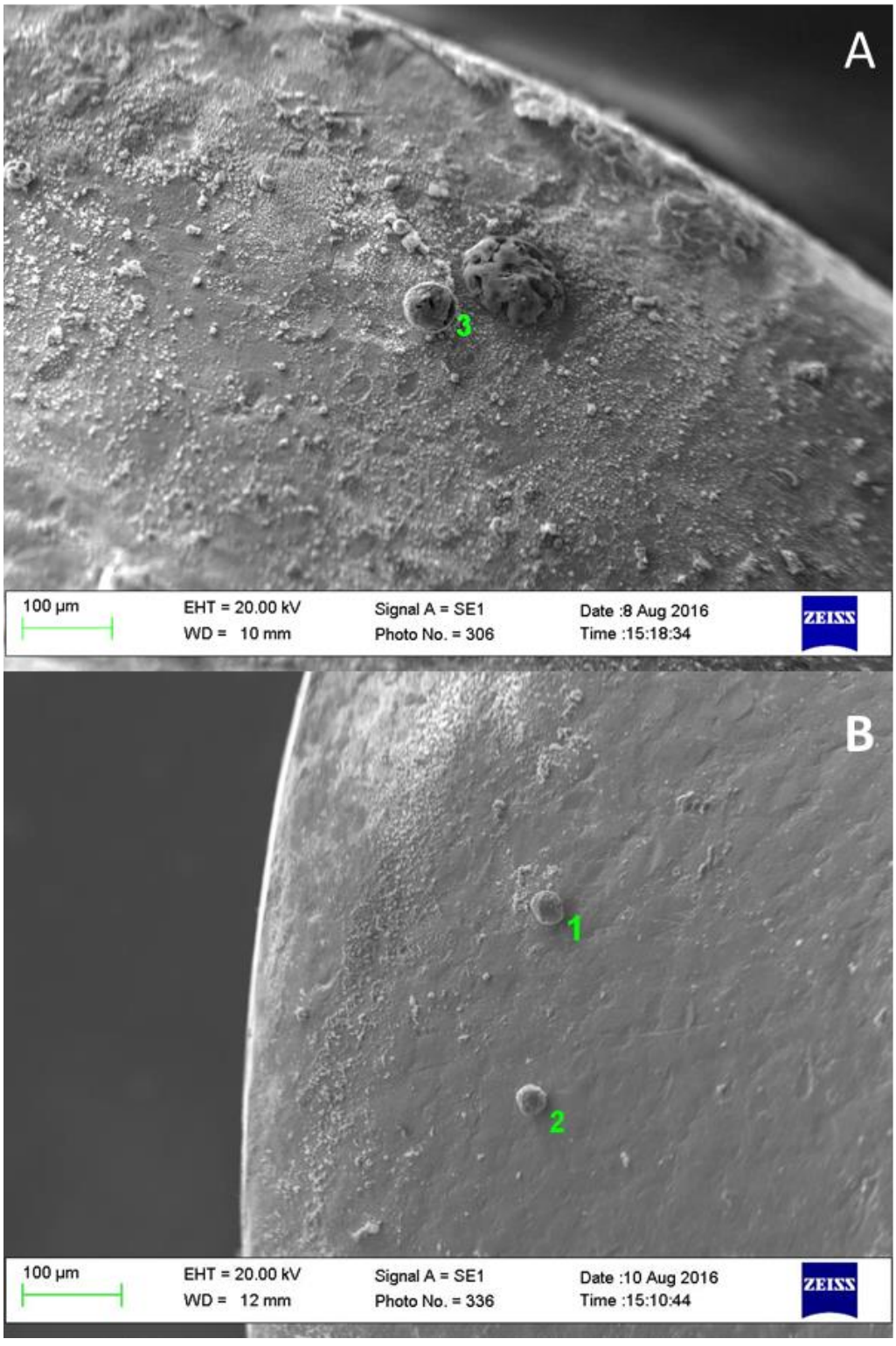


Figure 54: Liberty Lead-Free Anvils A) Full Cartridge B) Primed Only

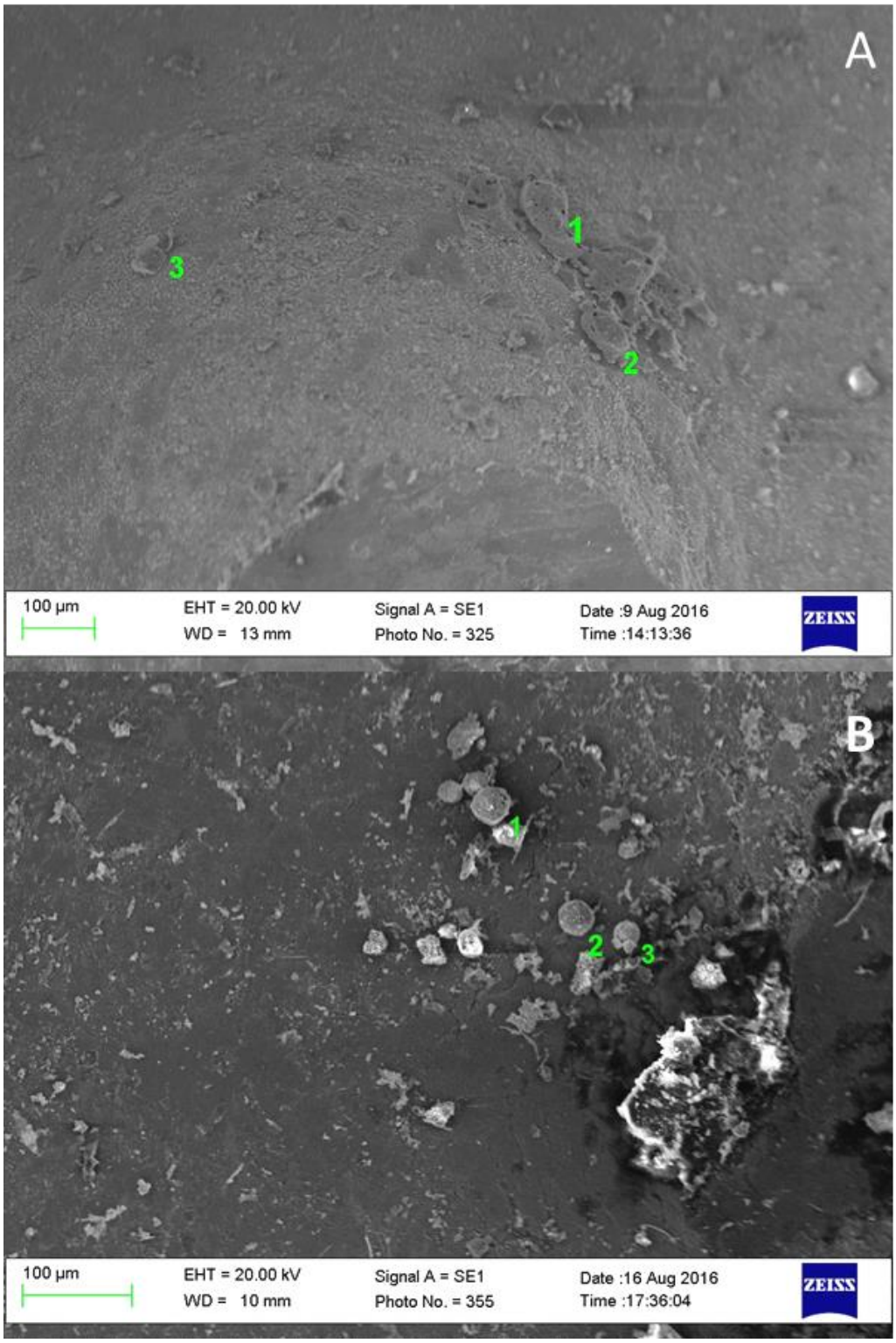


Figure 55: Liberty Lead- Free Cups A) Full Cartridge B) Primed Only

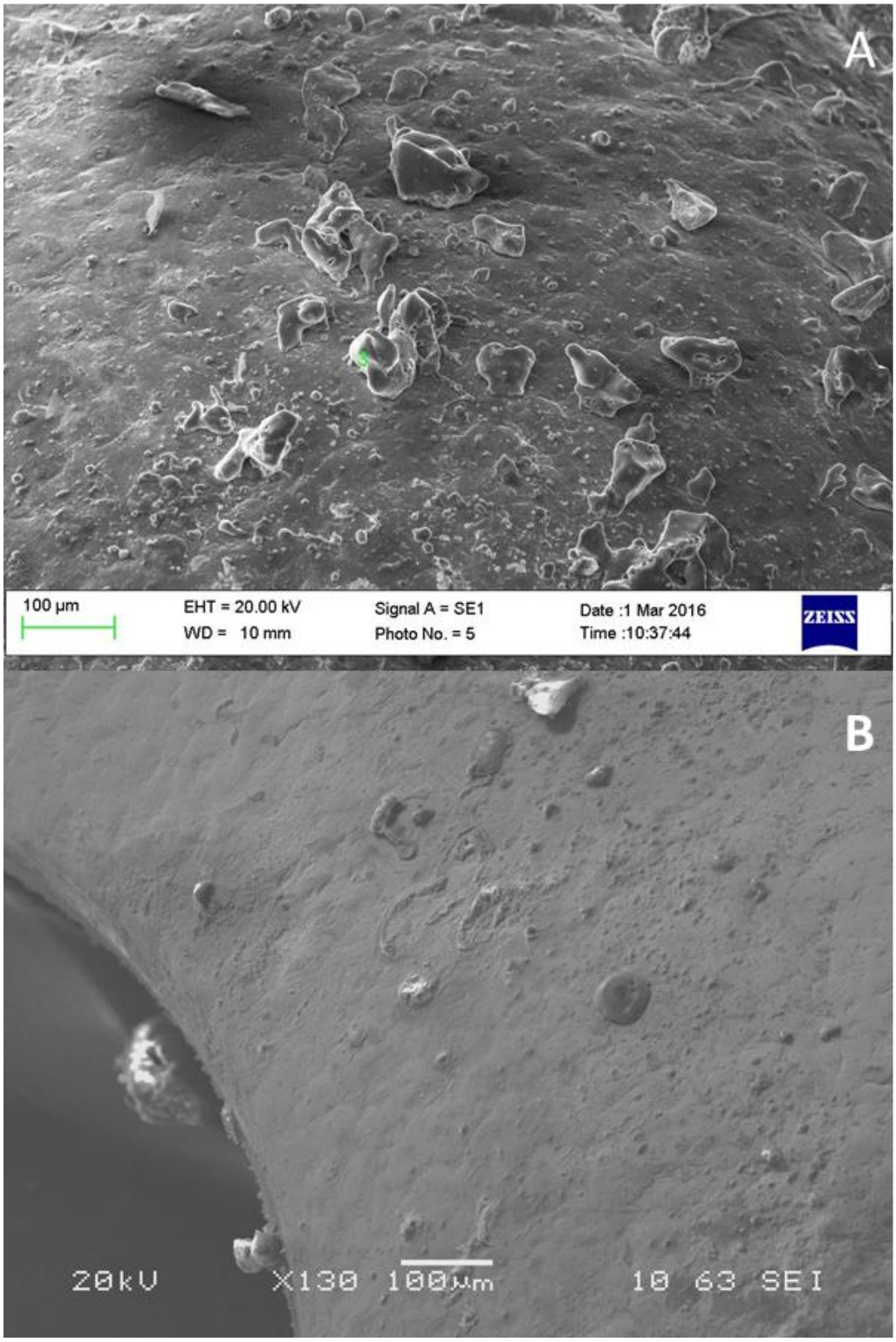


Figure 56: Sellier & Bellot Lead-Free Anvils A) Full Cartridge B) Primed Only

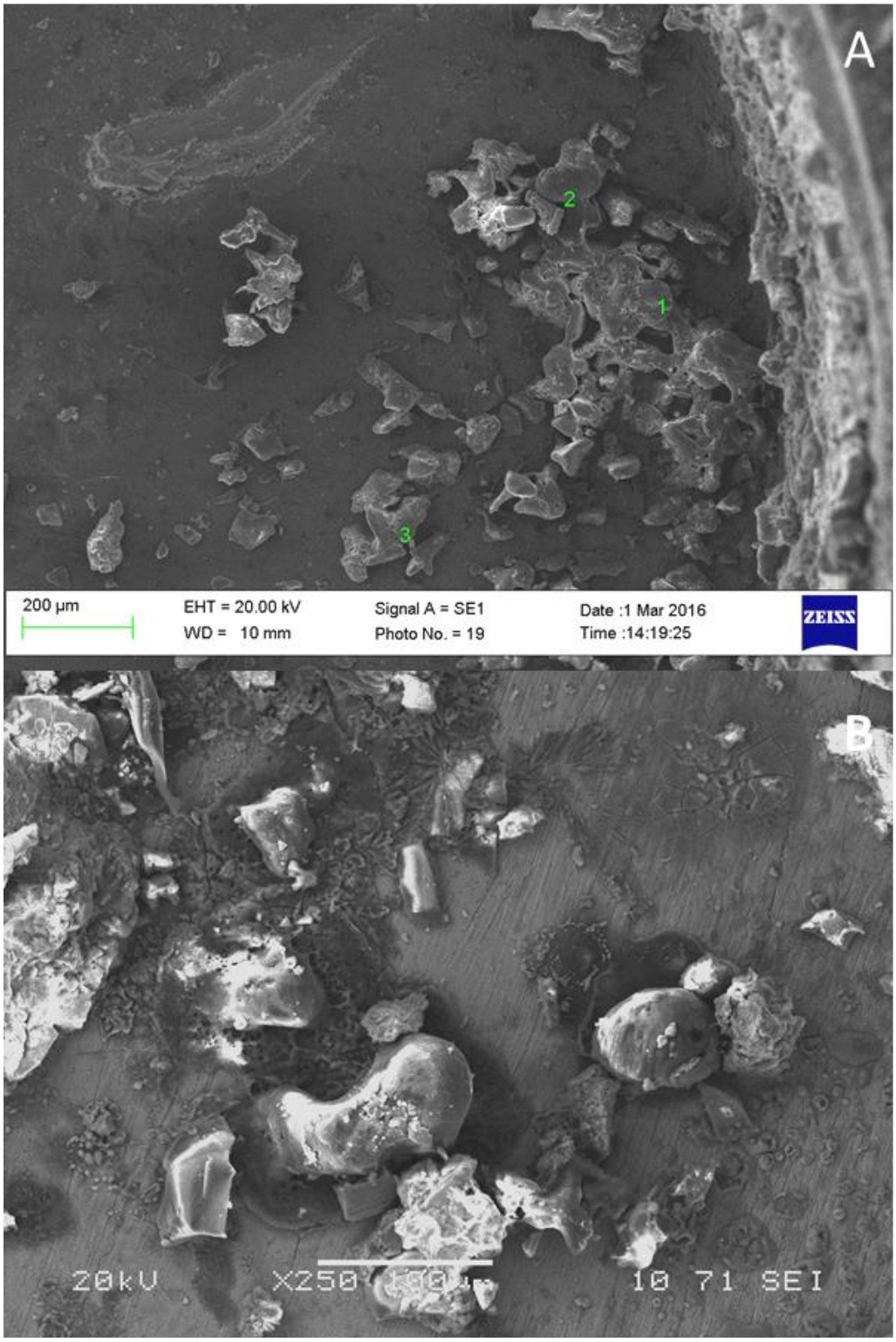


Figure 57: Sellier & Bellot Lead-Free Cups A) Full Cartridge B) Primed Only

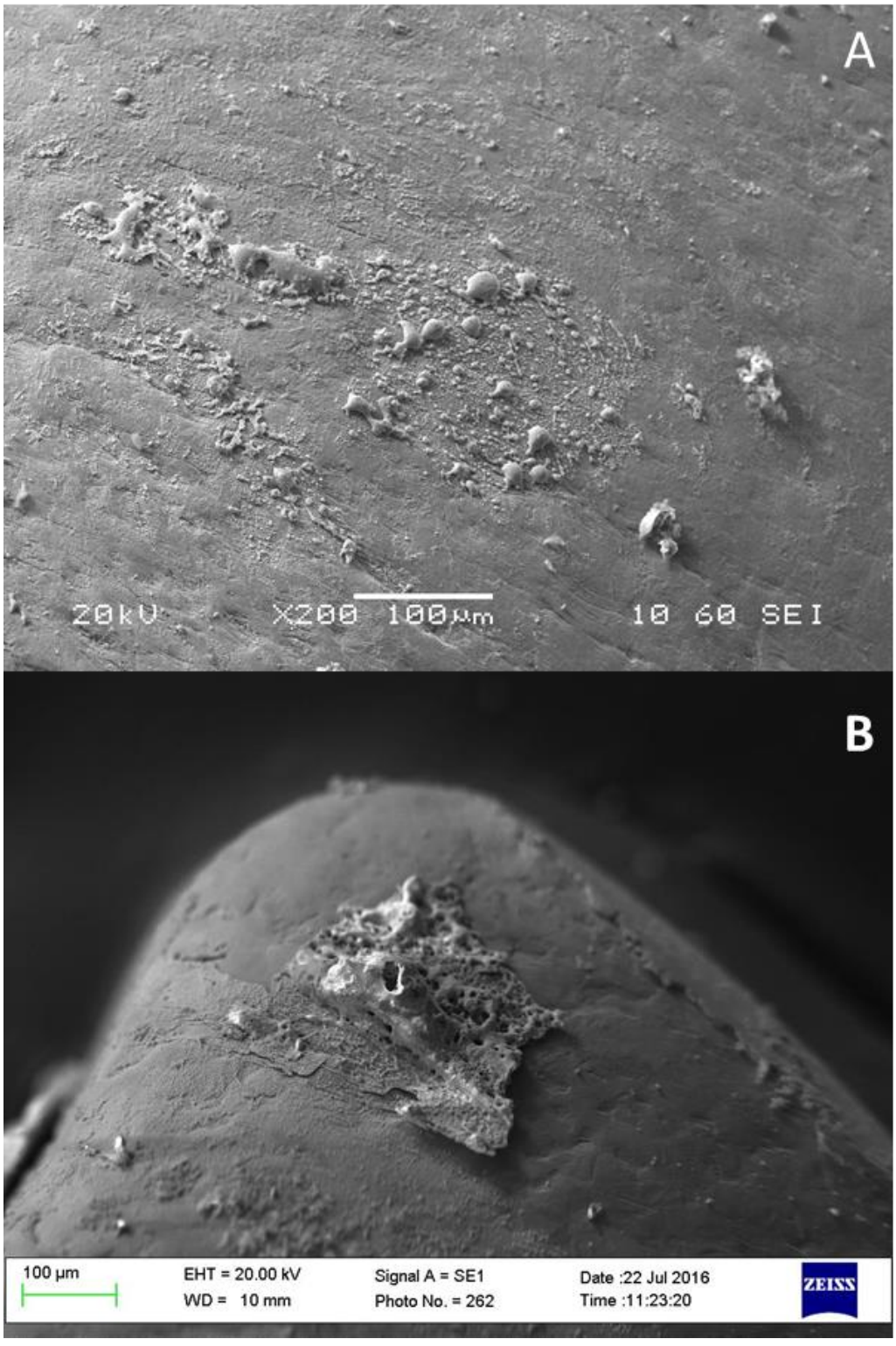


Figure 58: Sellier & Bellot Lead-Based Anvils A) Full Cartridge B) Primed Only

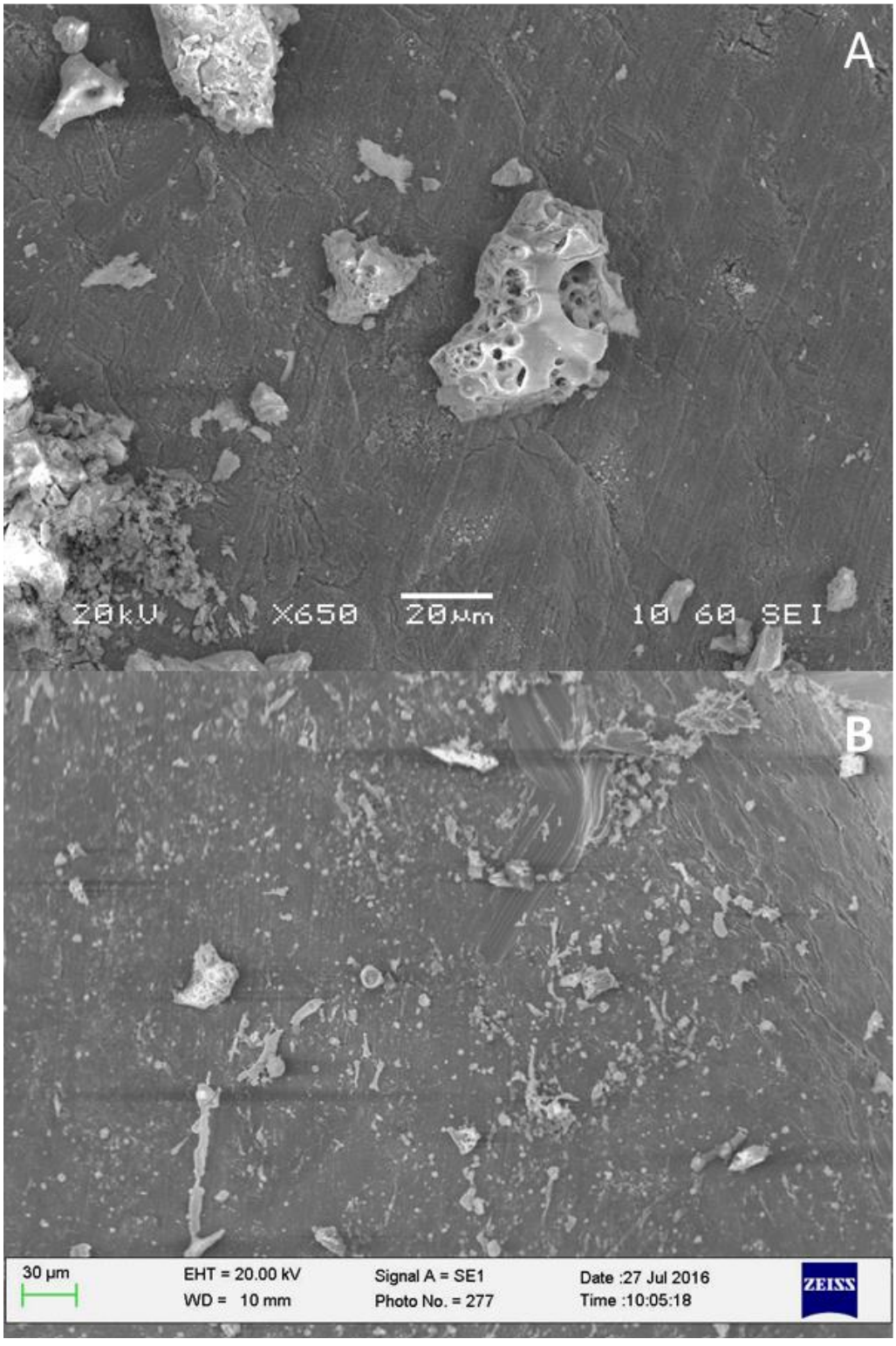


Figure 59: Sellier & Bellot Lead-Based Cups A) Full Cartridge B) Primed Only

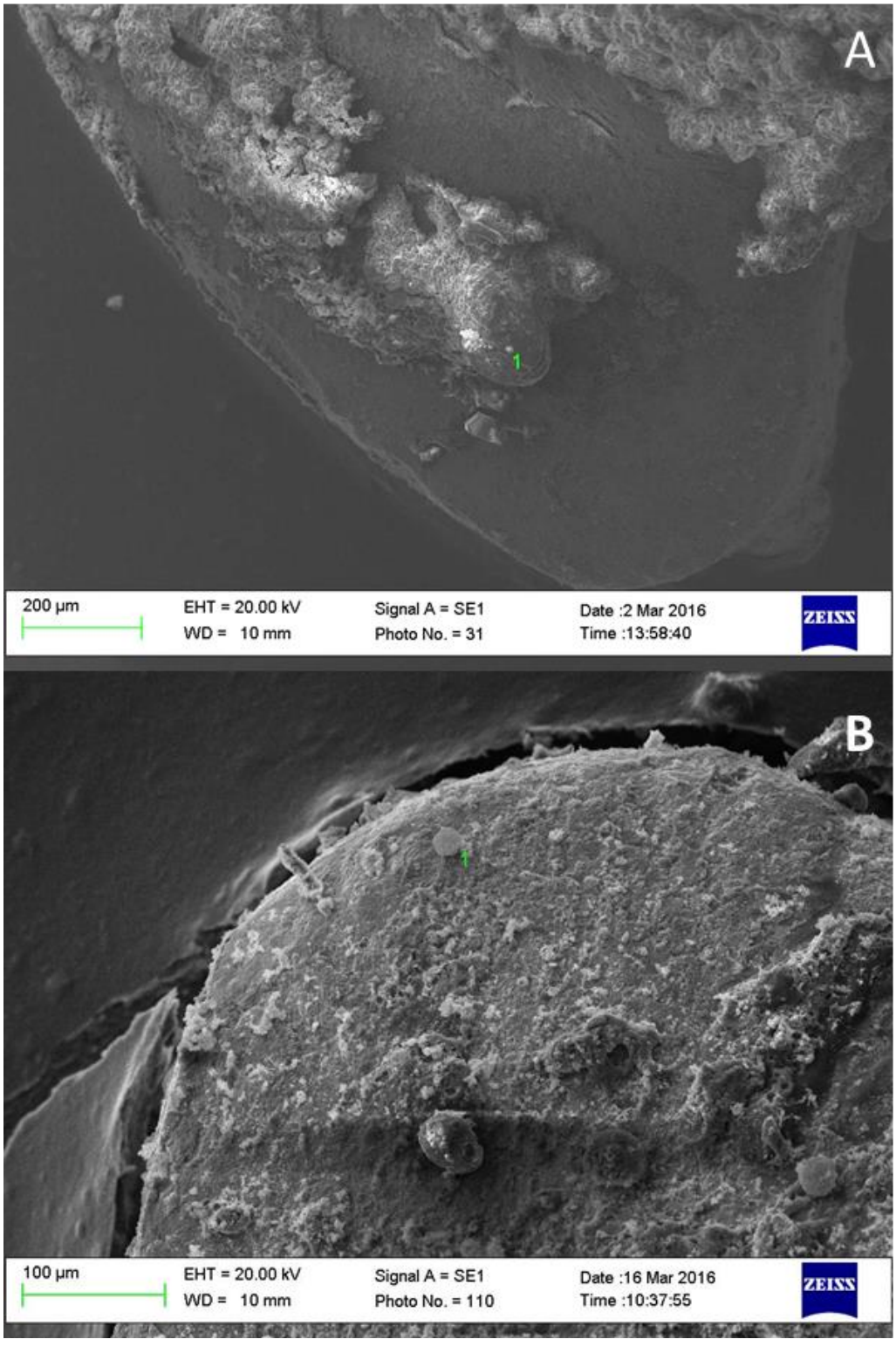


Figure 60: Winchester Lead-Free Anvils A) Full Cartridge B) Primed Only

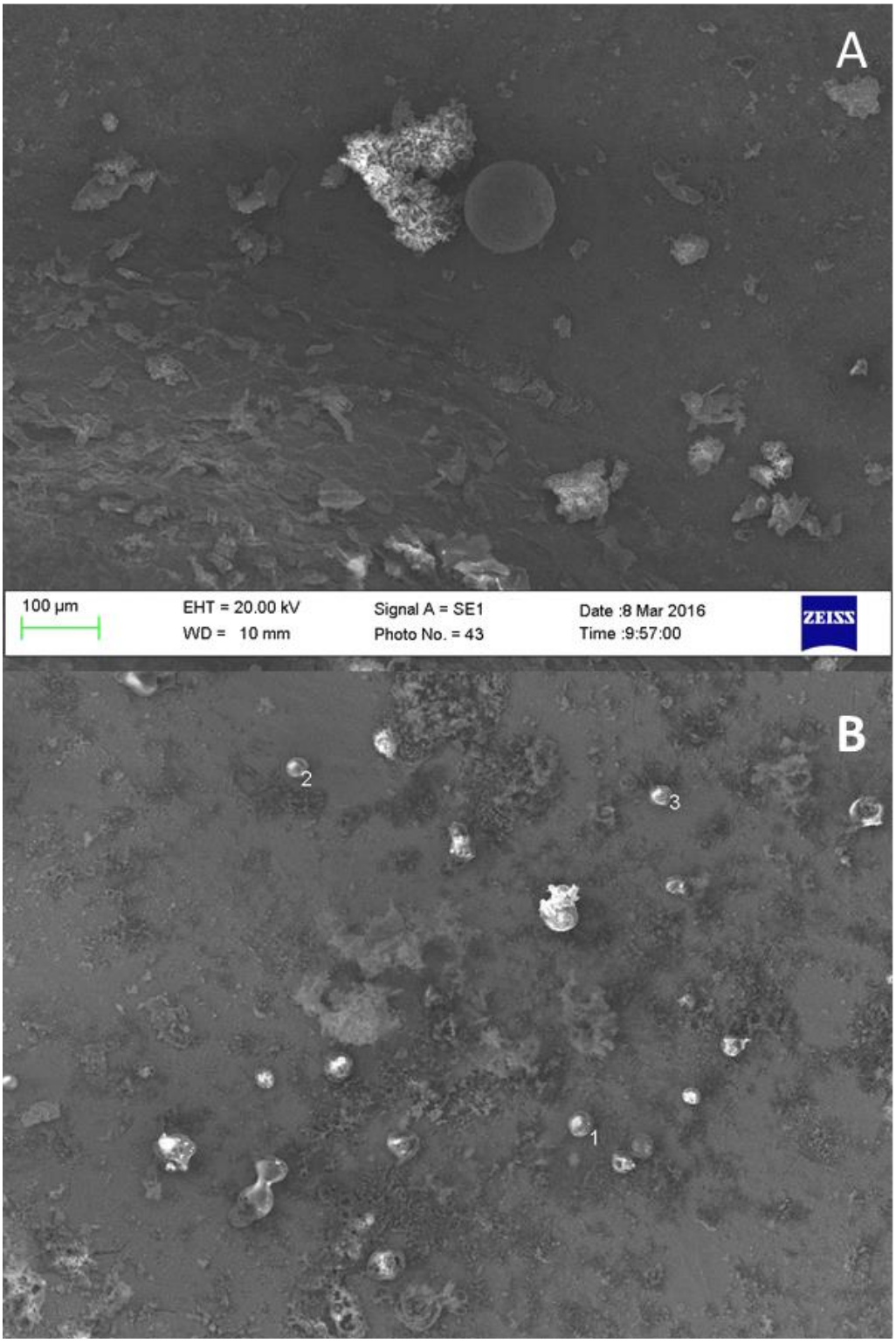


Figure 61: Winchester Lead-Free Cups A) Full Cartridge B) Primed Only

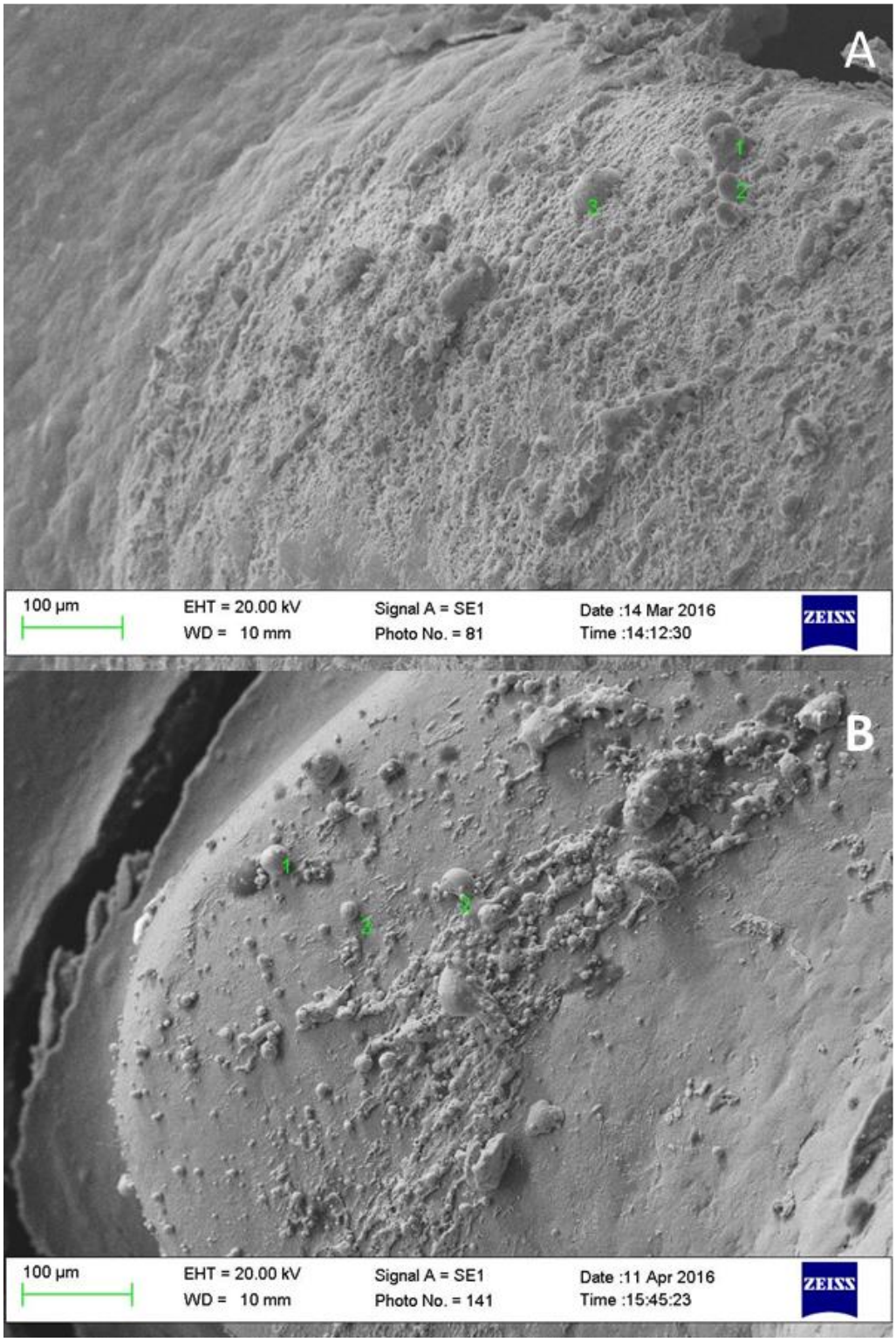


Figure 62: Winchester Lead-Based Anvils A) Full Cartridge B) Primed Only

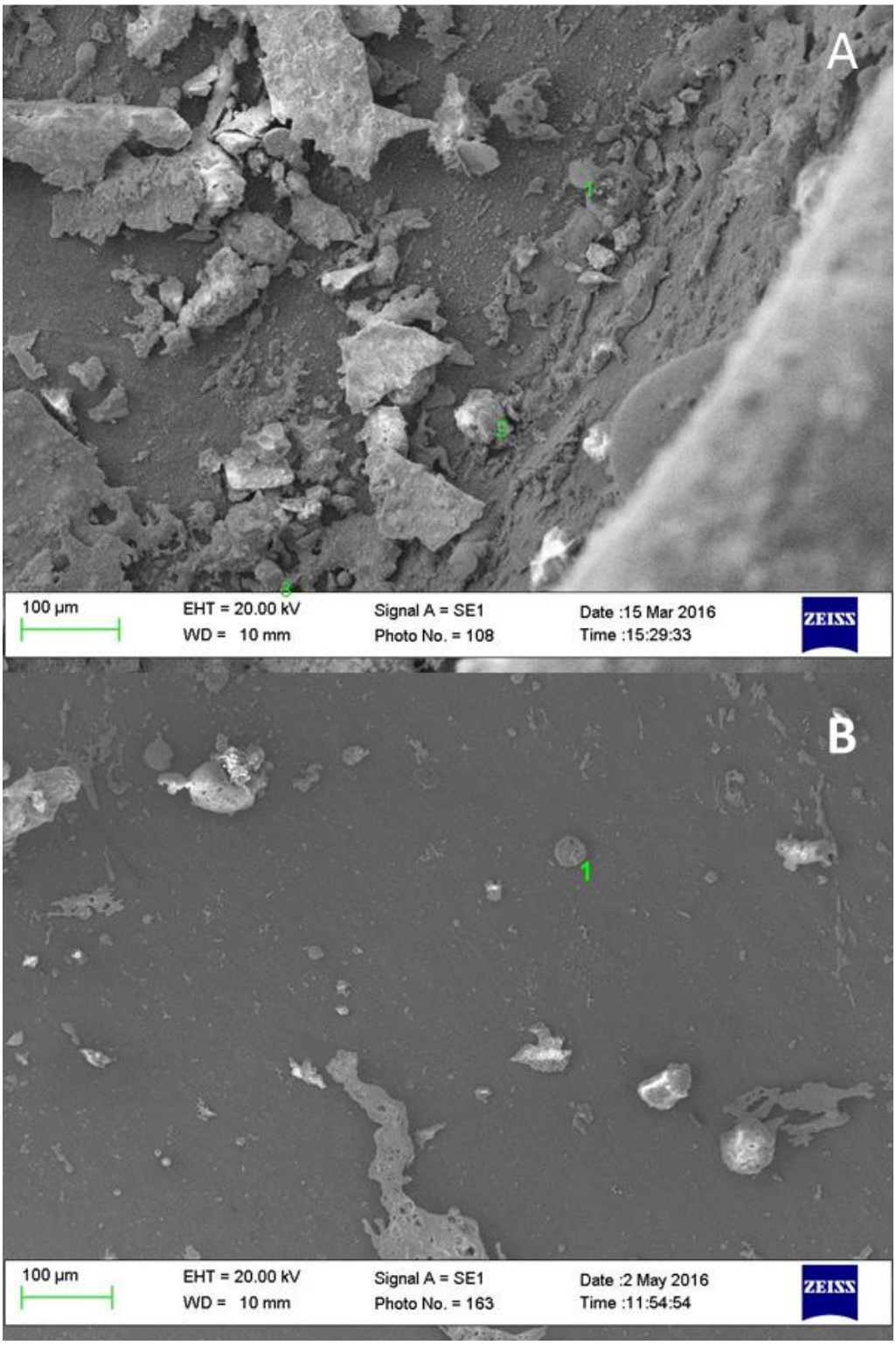


Figure 63: Winchester Lead-Based Cups A) Full Cartridge B) Primed Only

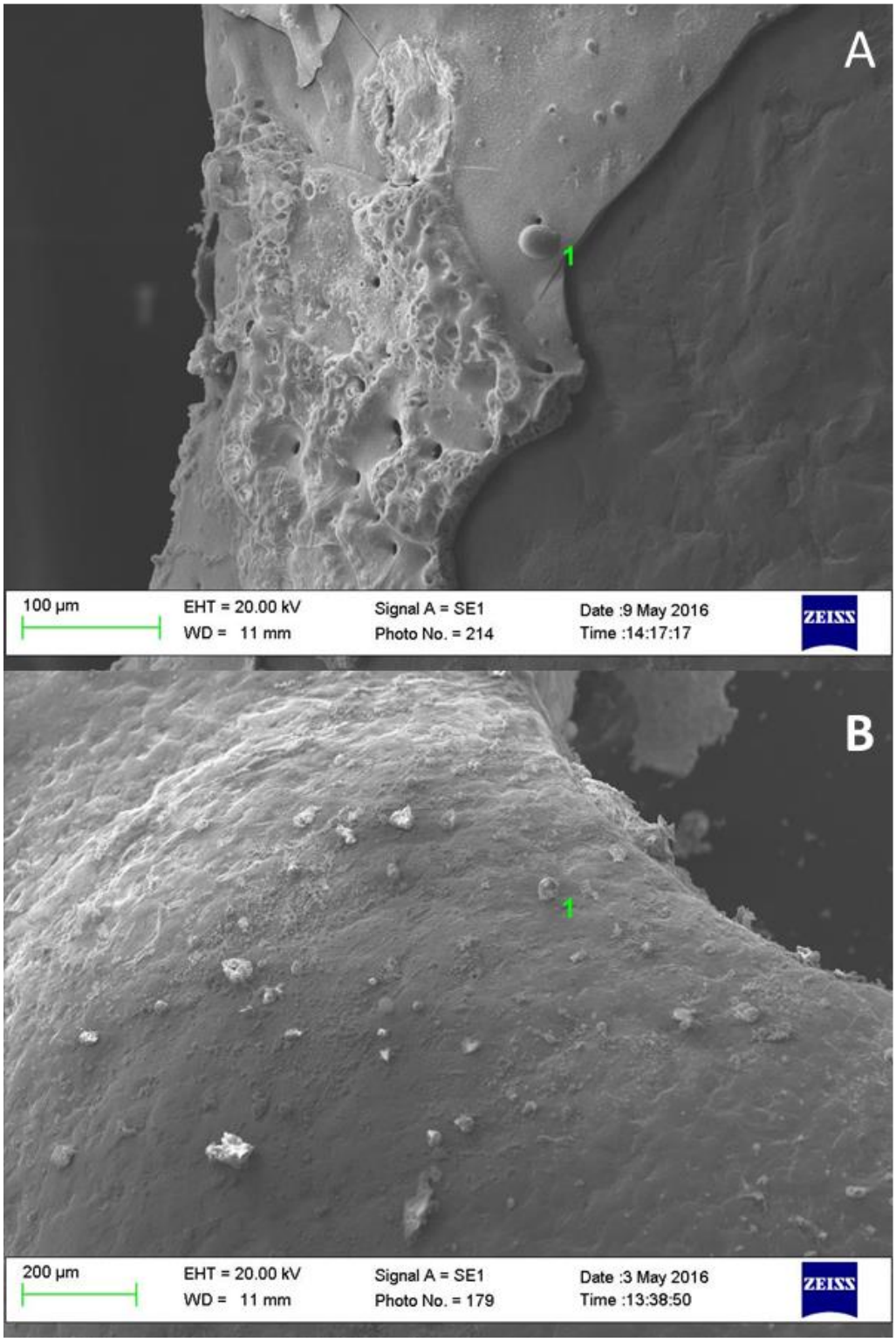


Figure 64: Liberty Lead-Based Anvils A) Full Cartridge B) Primed Only

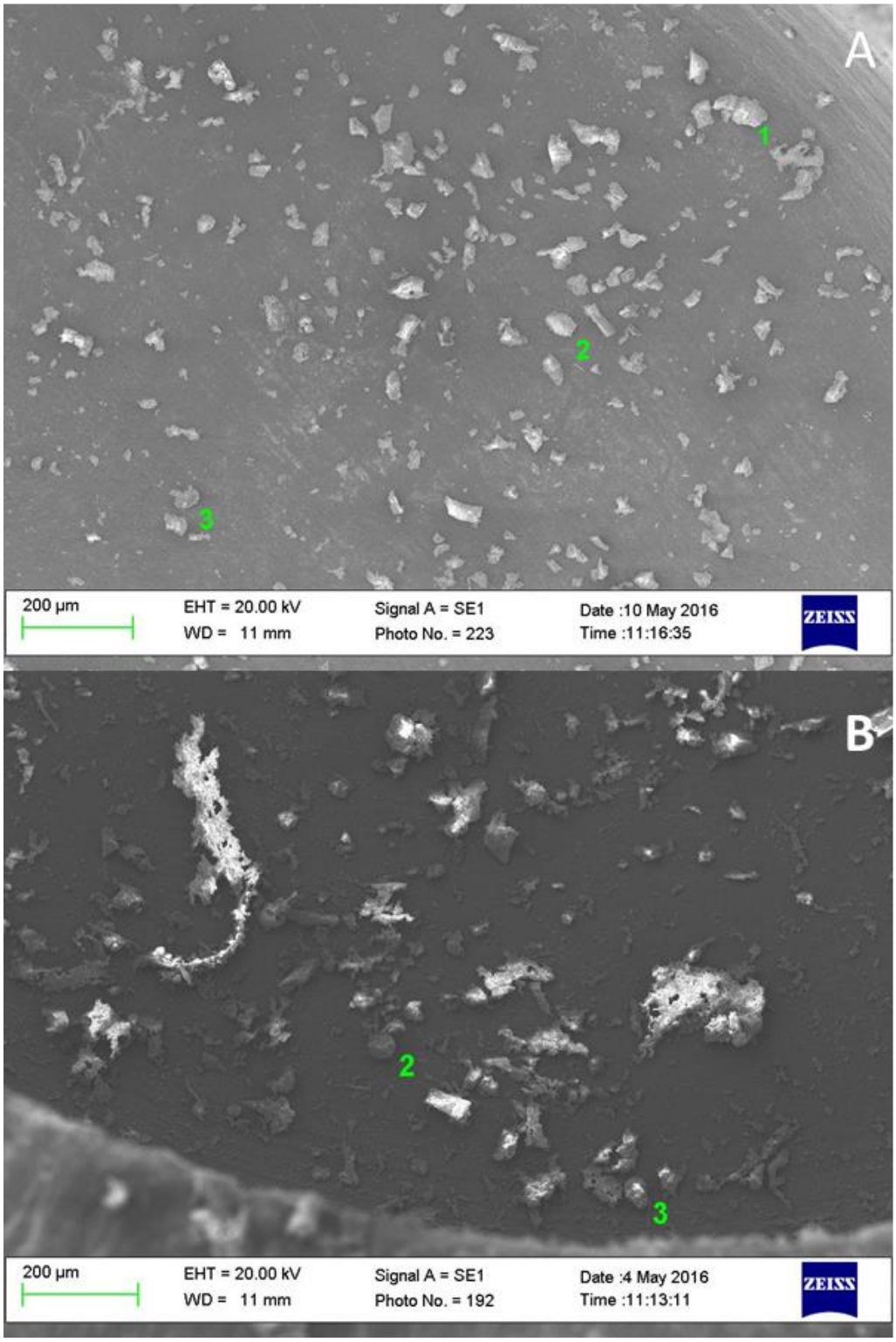


Figure 65: Liberty Lead-Based Cups A) Full Cartridge B) Primed Only

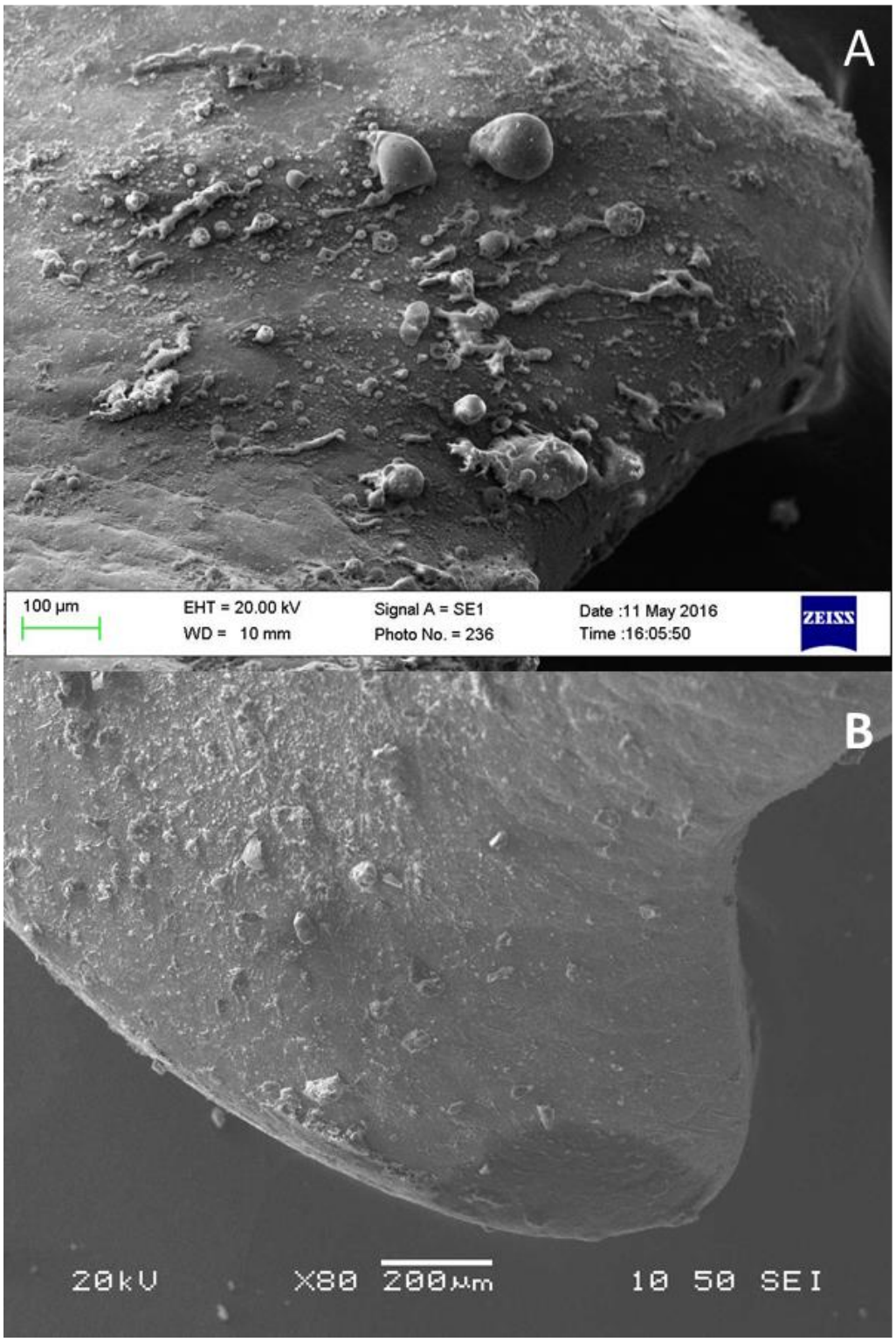


Figure 66: Federal Lead-Free Anvils A) Full Cartridge B) Primed Only

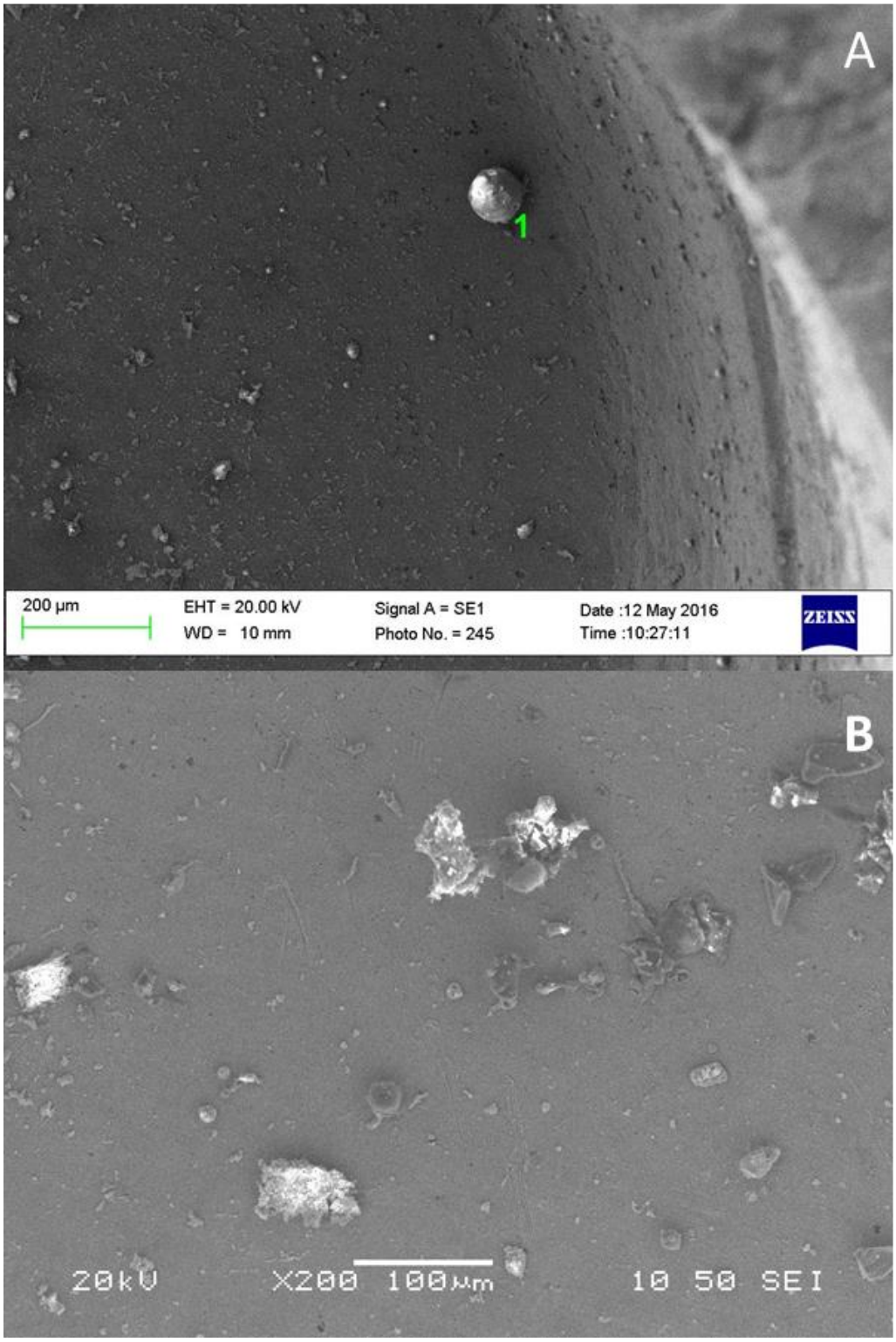


Figure 67: Federal Lead-Free Cups A) Full Cartridge B) Primed Only

APPENDIX C: SEM IMAGES MUZZLE DISCHARGE

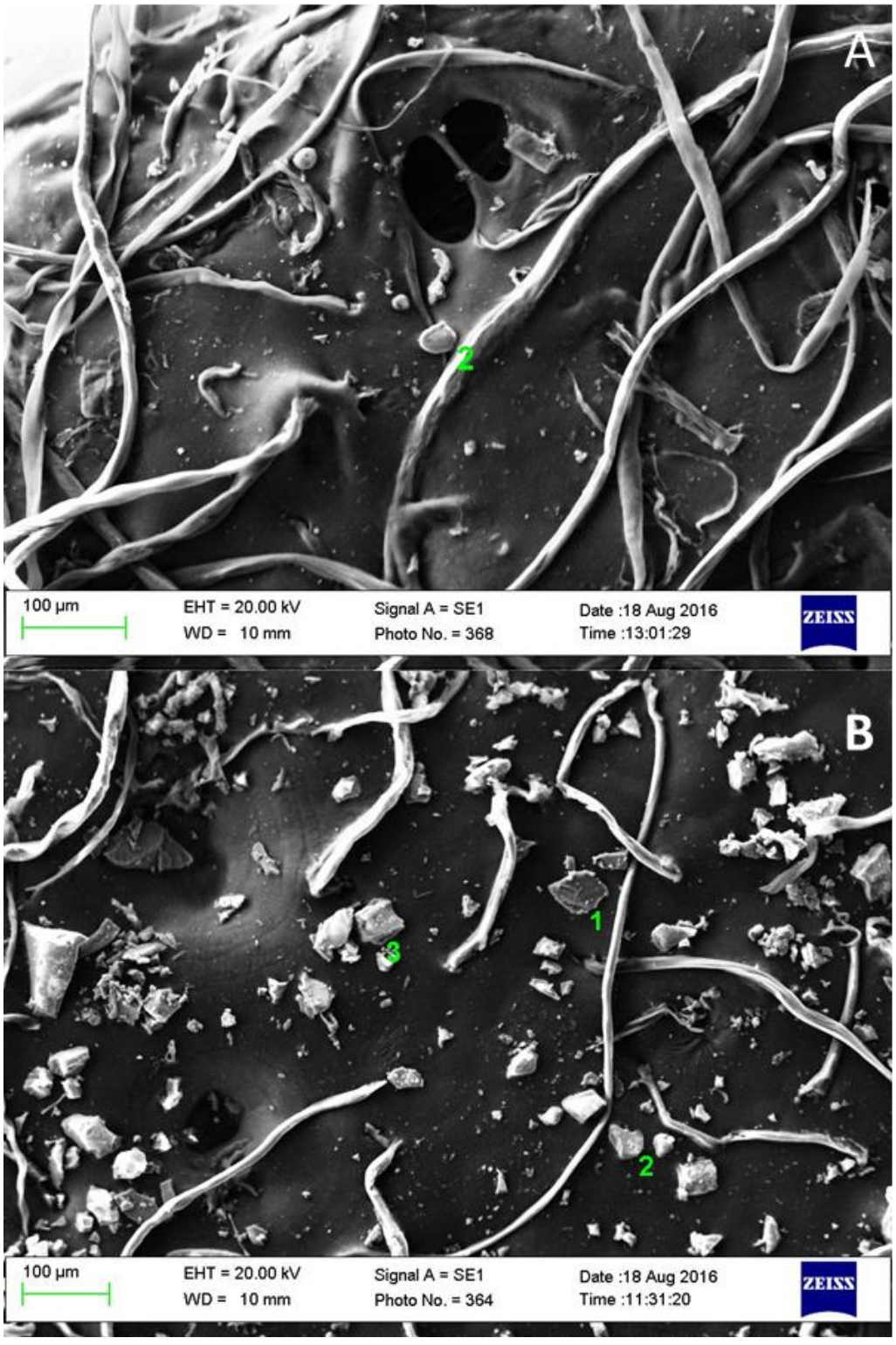


Figure 68: Sellier & Bellot Lead-Free Muzzle Discharge A) Full Cartridge B) Primed Only

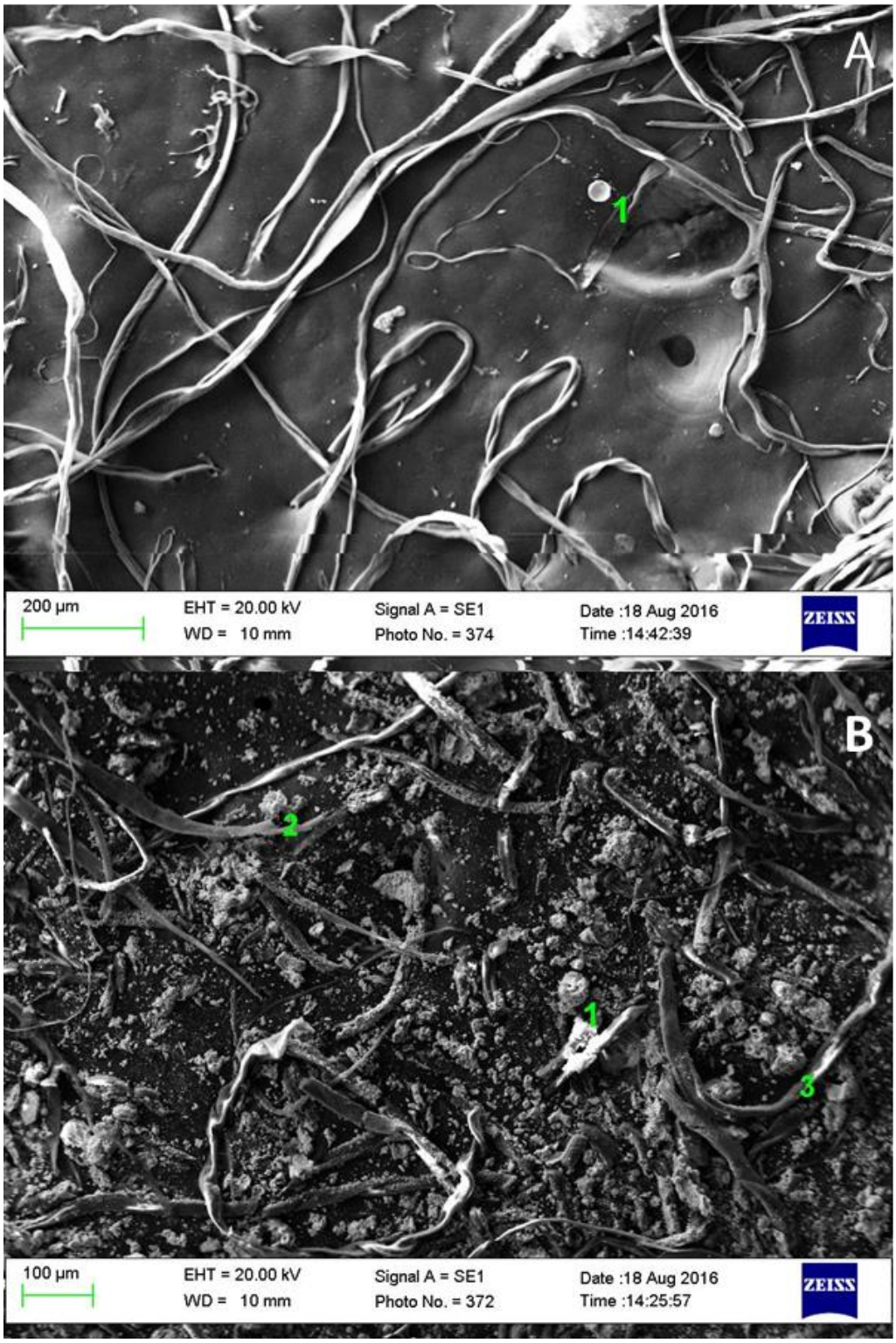


Figure 69: Winchester Lead-Based Muzzle Discharge A) FUll Cartridge B) Primed Only

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